VOL. XXVI. AUGUST, 1901. NO. 2.

AMERICAN

CHEMICAL JOURNAL

Contributions from the Chemical Laboratory of Cornell University.

THE CONSTITUTION OF GALLEÏN AND COERULEÏN.[1]

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I. GALLEÏN.

Galleïn was discovered by A. von Baeyer[2] in 1871. He made it by heating together phthalic anhydride and pyrogallol and, at first, regarded it as derived from pyrogallol by the loss of water according to the reaction

$$3C_6H_6O_3 = C_{18}H_{14}O_7 + 2H_2O.$$

Pyrogallol. Galleïn.

Later[3] he tried the action of phthalic anhydride on other phenols and found that they reacted in a similar manner. To the compounds resulting he gave the name phthaleïns, as he found that the phthalic anhydride took part in the reaction. From the analysis of phenolphthaleïn he concluded that it was made up of one residue of phthalic anhydride and two of phenol and represented the reaction thus:

$$C_8H_4O_3 + 2C_6H_6O = C_{20}H_{14}O_4 + H_2O.$$

Phthalic anhydride. Phenol. Phenolphthaleïn.

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[1] For the preliminary article on this subject see this JOURNAL, 23, 425.

[2] Ber. d. chem. Ges., 4, 457.

[3] *Ibid.*, 4, 658.

Resorcinphthaleïn, or fluoresceïn, he regarded as a double anhydride, representing the reaction as follows:

$$C_8H_4O_3 + 2C_6H_6O_2 = C_{20}H_{12}O_5 + 2H_2O.$$

Phthalic anhydride. Resorcin. Fluoresceïn.

The study of these reactions probably led him to change his views regarding the formation of galleïn, for in this article it is considered to be the phthaleïn of pyrogallol, being formed in accordance with the following equation:

$$C_8H_4O_3 + 2C_6H_6O_3 = C_{20}H_{12}O_7 + 2H_2O.$$

Phthalic anhydride. Pyrogallol. Galleïn.

The formula given for galleïn in the first paper, $C_{18}H_{14}O_7$, was found to be incorrect, owing to the property of the substance of forming a crystallized compound with alcohol. By purifying the galleïn without the use of alcohol, a product was obtained which gave, on analysis, results agreeing with the formula $C_{20}H_{12}O_7$. This view of the constitution of galleïn, that it is made up of two residues of pyrogallol combined with one of phthalic anhydride, he confirmed by showing that, on oxidation with nitric acid, galleïn yields, besides oxalic acid, phthalic acid in considerable quantity.

When the phthaleïns in alkaline solution are reduced with zinc dust, Baeyer found that the solution was almost immediately decolorized and that the phthaleïns were converted into their leuco compounds, which he designated *phthalins*. For phenolphthalin he determined the formula to be $C_{20}H_{16}O_4$, while to gallin, the phthalin of galleïn, he gave the formula $C_{20}H_{18}O_7$.

In this second paper on phenol dyes Baeyer suggests that phenolphthaleïn is formed in an analogous manner to sulphobenzid from benzene and sulphuric anhydride, as shown in the following equations:

$$C_8H_4O_3 + 2C_6H_6O = C_{20}H_{14}O_4 + H_2O;$$

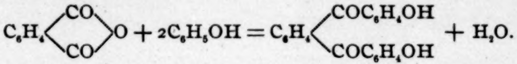
Phthalic anhydride. Phenol. Phenolphthaleïn.

$$SO_3 + 2C_6H_6 = C_6H_5SO_2C_6H_5 + H_2O.$$

Sulphuric anhydride. Benzene. Sulphobenzid.

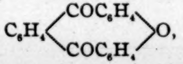
He adds, however, the following words, which are extremely interesting in view of the later conceptions of the constitution of the phthaleïns: "Wenn dieser Vorgang vielleicht dabei auch stattfindet, so ist er doch aller Wahrscheinlichkeit nach nicht der einzige, weil das Phthaleïn sich in Kalilauge mit prachtvoller Fuchsinfarbe löst und durch Zinkstaub in alkalischer Lösung entfärbt wird. Nach obiger Formel könnte diese Erscheinung nur durch das Verhalten der Acetongruppe hervorgerufen werden; nach den bisherigen Erfahrungen ist es aber wahrscheinlicher, das eine chinonartige Gruppe dazu Veranlassung giebt."

Fuoresceïn, on account of the beautiful fluorescence of its alkaline solutions and the fact that it is a yellow dyestuff, was the first of the phthaleïns to be closely investigated, and it is interesting to note in this connection that Emil Fischer's inaugural dissertation, published at Strassburg in 1874, was on fluoresceïn and orcinphthaleïn. In 1876 Baeyer published the first detailed account[1] of his investigations on the compounds of phthalic acid with the phenols. The reaction between phthalic anhydride and phenol he represents by the following equation:



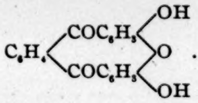
$$C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle O + 2C_6H_5OH = C_6H_4\left\langle\begin{matrix}COC_6H_4OH\\COC_6H_4OH\end{matrix}\right. + H_2O.$$

Fluoresceïn he regards as belonging to the group of the phthaleïn anhydrides, whose simplest representative is phenolphthaleïn anhydride,



$$C_6H_4\left\langle\begin{matrix}COC_6H_4\\COC_6H_4\end{matrix}\right\rangle O,$$

formed as a by-product in the preparation of phenolphthaleïn. The constitution of fluoresceïn must then, according to Baeyer, be expressed by the following formula:



$$C_6H_4\left\langle\begin{matrix}COC_6H_3\left\langle\begin{matrix}OH\\ \end{matrix}\right.\\ \\COC_6H_3\left\langle\begin{matrix}\\OH\end{matrix}\right.\end{matrix}\right\rangle O\ .$$

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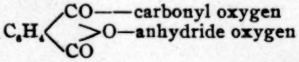
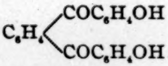
[1] Ann. Chem. (Liebig), 183, 2.

Vol. 2
190

In his second detailed paper[1] on the phthaleïns, published in 1880, Baeyer modified his views of the structure of these compounds very materially. In studying the action of fused caustic potash on phenolphthaleïn he found that one of the products was dioxybenzophenone. According to the diketone formula for phenolphthaleïn, the formation of dioxybenzophenone could only be explained by assuming a shifting of one of the phenol residues. If, however, we suppose that, in the formation of the phthaleïn, it is the carbonyl and not the anhydride oxygen, which is replaced by the two phenol residues, then the formation of dioxybenzophenone follows as a matter of course, as will be readily seen from the following formulas and equation:

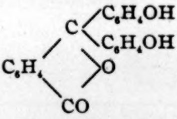


$$C_6H_4\left\langle\begin{matrix}CO\text{——carbonyl oxygen}\\ \quad >O\text{—anhydride oxygen}\\ CO\end{matrix}\right.$$

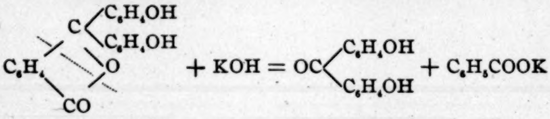


$$C_6H_4\left\langle\begin{matrix}COC_6H_4OH\\ COC_6H_4OH\end{matrix}\right.$$

Phenolphthaleïn.
(Diketone formula.)

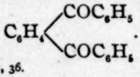


Phenolphthaleïn.
(New formula.)



Phenolphthaleïn. Dioxybenzophenone.

Further evidence in favor of the new formula for phenolphthaleïn was found in studying the phthalophenone of Friedel and Crafts. To this substance, made by the action of phthalyl chloride on benzene in the presence of aluminium chloride, had been assigned the following formula by the above-named authors:



$$C_6H_4\left\langle\begin{matrix}COC_6H_5\\ COC_6H_5\end{matrix}\right..$$

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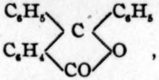
[1] Ann. Chem. (Liebig), 202, 36.

Baeyer found that it is in reality diphenylphthalid,



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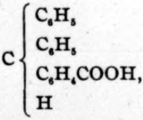
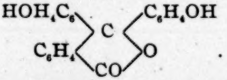
as it gave, on reduction in alkaline solution with zinc, triphenylmethanecarbonic acid,



$$C\begin{cases} C_6H_5 \\ C_6H_5 \\ C_6H_4COOH, \\ H \end{cases}$$

which, when heated with barium hydroxide, splits up into triphenylmethane and carbon dioxide. This same diphenylphthalid was converted into dinitrodiphenylphthalid by the action of nitric acid; on reduction, this gave diamidodiphenylphthalid, which with nitrous acid and water yielded dioxydiphenylphthalid, identical in every respect with phenolphthaleïn. The formula for phenolphthaleïn must hence be:



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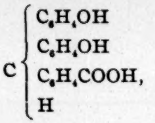
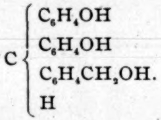
The position of the hydroxyl groups with reference to the methane carbon atom was assumed by Baeyer to be para, because substances in which the para position is occupied, such as parachlorphenol and paracresol, do not give phthaleïns, but phthaleïn anhydrides, while the ortho-substituted phenols give phthaleïns with the greatest ease. The formation of paradioxybenzophenone, when phenolphthaleïn is fused with caustic potash, is also in accord with this assumption.

To phenolphthalin, the product obtained from phenolphthaleïn by reduction in alkaline solution with zinc, Baeyer gives the formula



$$C\begin{cases} C_6H_4OH \\ C_6H_4OH \\ C_6H_4COOH, \\ H \end{cases}$$

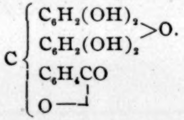
while phthalol, the product resulting from the phthalin by reduction in acetic acid solution with sodium amalgam, he represents as follows:



$$C\left\{\begin{array}{l} C_6H_4OH \\ C_6H_4OH \\ C_6H_4CH_2OH. \\ H \end{array}\right.$$

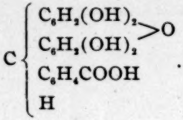
Gallin, the reduction-product of galleïn, corresponds, according to him, to this phthalol.

In 1881 K. Buchka[1] published his investigations on galleïn and coeruleïn. According to Buchka, Baeyer regarded galleïn, $C_{20}H_{12}O_7$, as a phthaleïn anhydride analogous to fluoresceïn, which it closely resembles. The following formula would therefore express its constitution:



$$C\left\{\begin{array}{l} \left.\begin{array}{l} C_6H_2(OH)_2 \\ C_6H_2(OH)_2 \end{array}\right> O. \\ C_6H_4CO \\ O \end{array}\right.$$

The formation of a tetracetate and a tetrabenzoate, indicating the presence of four hydroxyl groups in galleïn, is only an apparent confirmation of this formula, according to Buchka, as it is not possible to explain by it the conduct of galleïn toward reducing agents. Galleïn takes up 2 atoms of hydrogen when treated in alkaline solution with zinc dust, and if it had the above constitution it could only give a compound corresponding to phenolphthalin and having the following formula:



$$C\left\{\begin{array}{l} \left.\begin{array}{l} C_6H_2(OH)_2 \\ C_6H_2(OH)_2 \end{array}\right> O \\ C_6H_4COOH \\ H \end{array}\right.$$

A compound of this structure, however, must possess acid properties and yield, when treated with concentrated sulphuric acid, a product corresponding to phenolphthalidin. But galleïn, reduced in the cold according to Buchka, does not have acid properties and, though the reduced product dissolves in cold concentrated sulphuric acid, it is precipitated out again unchanged on the addition of water. By further reduction, however, this reduced product takes up two more atoms of hydrogen and is converted into a compound, which reacts strongly acid and is converted by sulphuric acid, even in the cold, into coerulin, corresponding to phenolphthalidin. This second reduction-product of galleïn must, therefore, according to Buchka, have a constitution corresponding to phenolphthalin and hence he calls it gallin. Buchka then took up the question as to the constitution of the substance intermediate between galleïn and gallin. He found that galleïn, reduced in alkaline solution in the cold with zinc dust, gave with acetic anhydride an acetate identical in all respects with the tetracetyl galleïn made from galleïn by heating it with acetic anhydride and sodium acetate. This remarkable result led him to assume that galleïn can take up 2 atoms of hydrogen without affecting the phthalic anhydride residue and that this hydrogen adds itself, in some way, to the two pyrogallol residues, which must be supposed to have suffered a partial oxidation in the preparation of galleïn. By assuming that in the formation of galleïn two of the hydroxyl groups belonging to the pyrogallol residues form a quinone group in a way analogous to the formation of cedriret,

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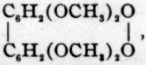
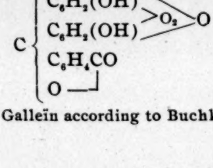
[1] Ann. Chem. (Liebig), 209, 251.



$$\begin{array}{l} C_6H_2(OCH_3)_2O \\ | \qquad\qquad\qquad | \\ C_6H_2(OCH_3)_2O \end{array},$$

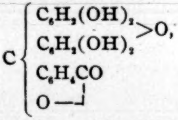
by the oxidation of the dimethyl ether of pyrogallol, he arrives at the following formula for galleïn:



$$C\left\{\begin{array}{l} C_6H_2(OH) \\ C_6H_2(OH) \\ C_6H_4CO \\ O \end{array}\right. \!\!>O_2>O$$

Galleïn according to Buchka.

When reduced in the cold, a compound of this formula would, according to him, take up 2 atoms of hydrogen, the quinone group being first reduced, and the product formed, which he calls hydrogalleïn,

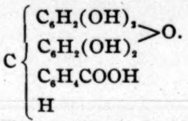


$$C\left\{\begin{array}{l}\left.\begin{array}{l}C_6H_3(OH)_2\\ C_6H_3(OH)_2\end{array}\right\rangle O,\\ C_6H_4CO\\ O-\!\!\rfloor\end{array}\right.$$

Hydrogalleïn, according to Buchka.

would not have the character of an acid nor could it be converted by the action of sulphuric acid into a phthalidin. On the other hand, this compound would give a tetracetyl derivative. He states that the formation of this same tetracetyl product from galleïn itself might be regarded as an argument against the assumption of a quinone group in galleïn, since we should naturally expect here the formation of only a diacetyl galleïn. The analyses of both products, however, proved the presence of four acetyl groups and, moreover, the properties of this galleïn tetracetate do not accord with the assumption of the presence of a quinone group. We must, therefore, according to him, if we hold to the assumption of a quinone bond or union in galleïn, suppose a breaking of this union in the formation of the tetracetyl galleïn. Quinone, and chloranil act in an analogous manner. Thus Sarauw obtained diacetyl hydroquinone by the action of acetic anhydride and sodium acetate on quinone and Graebe made diacetyltetrachlorhydroquinone by heating chloranil with acetyl chloride. The quinone union may therefore be broken by an acid anhydride or an acid chloride, though with difficulty, and the taking up of four acid residues in the formation of tetracetyl galleïn is not contrary to the assumption of a quinone group in galleïn. From this reasoning Buchka concludes that galleïn does not have the formula $C_{20}H_{12}O_7$, last assigned to it by Baeyer, but one containing 2 atoms of hydrogen less, $C_{20}H_{10}O_7$.

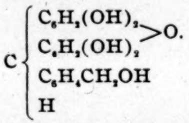
On further reduction of the hydrogalleïn, $C_{20}H_{12}O_7$, there is formed the compound corresponding to phenolphthalin:



$$C\left\{\begin{array}{l} \left.\begin{array}{l} C_6H_2(OH)_2 \\ C_6H_2(OH)_2 \end{array}\right> O. \\ C_6H_4COOH \\ H \end{array}\right.$$

Gallin, according to Buchka.

This compound Buchka calls gallin, a name which Baeyer originally gave to the last reduction-product of galleïn, corresponding to phthalol, which Buchka designates gallol. To this gallol he assigns the formula

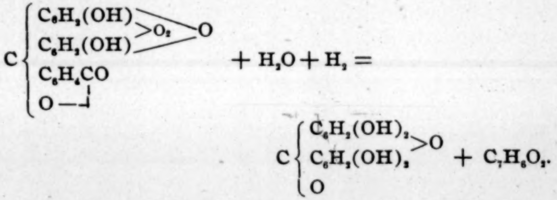


$$C\left\{\begin{array}{l} \left.\begin{array}{l} C_6H_2(OH)_2 \\ C_6H_2(OH)_2 \end{array}\right> O. \\ C_6H_4CH_2OH \\ H \end{array}\right.$$

Gallol, according to Buchka.

Gallin, he found to give with acetic anhydride a tetracetyl, and gallol a pentacetyl, derivative.

By fusing with alkalies, Buchka found that galleïn is split up in an analogous manner to phenolphthaleïn. It gives, besides benzoic acid, the anhydride of pyrogallol ketone by taking up 2 atoms of hydrogen. He represents the reaction as follows:



$$C\left\{\begin{array}{l} \left.\begin{array}{l} C_6H_2(OH) \\ C_6H_2(OH) \end{array}\right> O_2 > O \\ C_6H_4CO \\ O\text{—} \end{array}\right. + H_2O + H_2 =$$

$$C\left\{\begin{array}{l} \left.\begin{array}{l} C_6H_2(OH)_2 \\ C_6H_2(OH)_2 \end{array}\right> O \\ O \end{array}\right. + C_7H_6O_2.$$

In 1892 Herzig[1] repeated a part of Buchka's work on galleïn and obtained results which do not agree with those given by Buchka. The formation of colorless acetyl derivatives of quercetin and ethyl quercetin, etc., made it appear possible to Herzig that these colorless products were not acetyl derivatives of the original dyestuffs, but of their leuco compounds, especially since Graebe and Caro[1] had already obtained, by the action of acetic anhydride on rosolic acid, not acetyl rosolic acid but the acetyl derivative of leucorosolic acid. The melting-points of acetyl phenolphthaleïn and acetyl phenolphthalin, as given by Baeyer (143° and 146°), are very nearly the same, and preliminary experiments showed that acetyl fluoresceïn and acetyl fluorescin melted at practically the same point (200° to 201° and 200° to 202°). This suggested to Herzig the idea that phenolphthaleïn and fluoresceïn give with acetic anhydride acetyl phenolphthalin and acetyl fluorescin, reduction as well as acetylization taking place. This idea did not prove correct, however, for while acetyl fluoresceïn and acetyl fluorescin have the same melting-point they differ very markedly in their conduct towards dilute alkali solutions. Acetyl fluoresceïn dissolves in dilute alkalies only in so far as it is saponified and even after some hours undissolved acetyl fluoresceïn may be regained by filtration. Acetyl fluorescin, on the other hand, dissolves very readily in dilute alkalies in the cold and if the solution is quickly acidified it may be regained unsaponified with the melting-point 200° to 202°. The same difference is shown by acetyl phenolphthaleïn and acetyl phenolphthalin and is a necessary consequence of the constitution of the phthaleïn and phthalin.

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[1] Monatsh Chem., 13, 425.

Herzig then calls attention to the fact that Buchka claims to have obtained, by reduction, a product, hydrogalleïn, intermediate between galleïn and gallin. Acetyl gallin he found to be an acid, and hence gallin bears the same relation to galleïn that fluorescin does to fluoresceïn. Hydrogalleïn, however, is said to yield the same acetyl product as galleïn itself, and from this fact Buchka concludes that two quinone-oxygen atoms are present in galleïn. Owing to the importance of this observation for the constitution of galleïn and that Buchka does not describe the conduct of the two acetyl products towards dilute alkalies, Herzig thought it advisable to repeat this part of Buchka's work. He first made tetracetyl galleïn and found that it melted, when recrystallized from benzene, at 234° to 237°. Buchka gives it the melting-point 247° to 248°. This difference caused Herzig to repeat the preparation of his acetyl galleïn. He obtained a product with the same melting-point, 236° to 237°. From this acetyl galleïn he made pure galleïn by saponification. This he reduced with caustic potash and zinc dust in the cold exactly as Buchka directs. The product had the appearance and properties of hydrogalleïn but it gave with acetic anhydride not acetyl galleïn but a substance which, when recrystallized from benzene, melted at 210° to 213°. Moreover, it differed from acetyl galleïn soluble in caustic alkali without saponification, which is naturally not the case with acetyl galleïn. This product Herzig assumes to be the tetracetyl gallin, which, according to Buchka, melts at 220°. Owing to this difference in melting-point, Herzig repeated the reduction experiment, avoiding all heating and working so that the entire reaction was ended in a quarter of an hour. Notwithstanding all these precautions, however, the product had the same melting-point (211° to 213°). Herzig concludes his article with the following words: "Buchka scheint nach seiner Beschreibung eine grössere Menge des Hydrogalleïns in der Hand gehabt zu haben, und es können daher meine beiden negativen Befunde vorläufig die Existenz desselben nicht in Frage stellen. Allerdings glaube ich, dass die Darstellung des Hydrogalleïns nicht so einfach ist, wie sie Buchka beschreibt und dass noch andere Vorsichtsmassregeln nothwendig sind, die der genannte Autor entweder nur unbewusst eingehalten oder in seiner Arbeit zu erwähnen vergessen hat. Ebenso halte ich es vorläufig nicht für ausgeschlossen, dass die Identität der Acetylproducte des Galleïns und Hydrogalleïns nur auf Grund der Schmelzpunkte ausgesprochen wurde, während sie sich in Bezug auf die Löslichkeit in Alkalien von einander so unterscheiden können, wie Acetylfluoresceïn von Acetylfluorescin."

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[1] Ann. Chem. (Liebig), **179**, 198.

For some years previous to this date (1892) the views of chemists as to the chemical nature of colored organic compounds, the cause of their color, and the relation of this physical property to their chemical constitution had undergone important changes.[1] These colored compounds, which had been considered as derivatives of benzene and related hydrocarbons, were coming more and more to be regarded as derivatives of the dihydro addition-products of these hydrocarbons; *i. e.*, as quinone-like compounds or as having a quinoid structure, the quinones themselves being considered as para- or orthodiketones.

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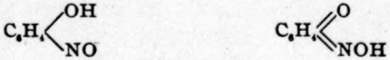
[1] See in this connection H. E. Armstrong's paper "On the Origin of Color." Proc. Chem. Soc., 1887–1888, No. 49, p. 27.

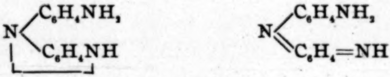
The relation between the old and the new ideas regarding the constitution of colored organic compounds will be readily seen from the following formulas :

Old formula. New (quinoid) formula.



$$C_6H_4\left\langle\begin{matrix}OH\\NO\end{matrix}\right. \qquad C_6H_4\left\langle\!\!\left\langle\begin{matrix}O\\NOH\end{matrix}\right.\right.$$

Nitrosophenols.



$$N\left\langle\begin{matrix}C_6H_4NH_2\\C_6H_4NH\end{matrix}\right. \qquad N\left\langle\begin{matrix}C_6H_4NH_2\\ \| C_6H_4{=}NH\end{matrix}\right.$$

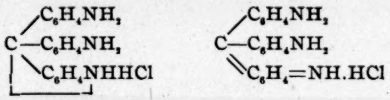
Indamine.

$C_6H_5N_2C_6H_4OH$ $C_6H_5NHN{=}C_6H_4{=}O$

Oxyazobenzene.

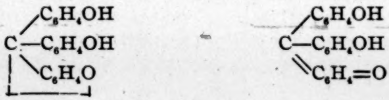
$C_6H_5N_2C_6H_4NH_2$ $C_6H_5NH.N{=}C_6H_4{=}NH$

Amidoazobenzene.



$$C\left\langle\begin{matrix}C_6H_4NH_2\\C_6H_4NH_2\\C_6H_4NHHCl\end{matrix}\right. \qquad C\left\langle\begin{matrix}C_6H_4NH_2\\C_6H_4NH_2\\ \| C_6H_4{=}NH.HCl\end{matrix}\right.$$

Pararosaniline hydrochloride.



$$C\left\langle\begin{matrix}C_6H_4OH\\C_6H_4OH\\C_6H_4O\end{matrix}\right. \qquad C\left\langle\begin{matrix}C_6H_4OH\\C_6H_4OH\\ \| C_6H_4{=}O\end{matrix}\right.$$

Aurin.

In 1892 A. Bernthsen[1] put forward certain very interesting and important speculations as to the structure of the phthaleïns in an address before the Chemical Society at Heidelberg on the constitution of the rhodamines and eosines.

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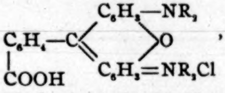
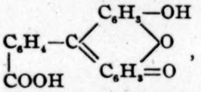
[1] Chem. Ztg., 104, 1956 (1892).

After proving that the constitution of rhodamine hydrochloride is correctly represented by the formula



Rhodamine hydrochloride.

he assumes an analogous constitution for the corresponding hydroxyl dyes; for example, he gives fluoresceïn in its salts the formula

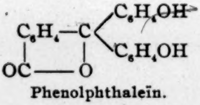


Fluoresceïn in its salts.

while for the free fluoresceïn, which yields a diacetyl product, the lactone formula of Baeyer is retained. The fact that fluoresceïn gives an easily saponifiable ethyl derivative (an ester), which may also be made by oxidation of the colorless fluorescin ethyl ester, is the chief argument in favor of the above formula.

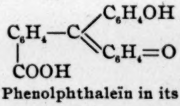
It is very probable also, according to Bernthsen, that the characteristic color change of phenolphthaleïn with an alkali is to be explained by assuming that the colorless compound has the lactone formula (I.), but in the violet-red salts the quinoid formula (II.):

I.



Phenolphthaleïn.

II.

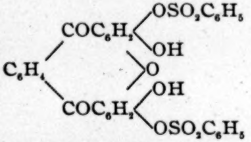


Phenolphthaleïn in its salts.

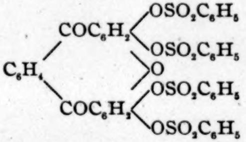
Since the publication of this address of Bernthsen, much work has been done on the phthaleïns with a view to determining their constitution. The phthaleïns are now generally regarded as tautomeric substances, since they yield both colorless and colored derivatives. The colorless compounds are given the lactoid[1] structure, while the colored products are considered to be quinoid derivatives.

While much work has been done on phenolphthaleïn and fluoresceïn and their constitution has been fully determined, galleïn has been neglected since Buchka published the results of his investigations.

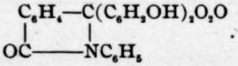
M. Georgescu[2] has made the dibenzene- and tetrabenzenesulphonates by treating alkaline solutions of galleïn with benzene sulphonchloride and given them the formulas



and

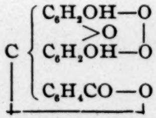


and Albert[3] the galleïn anilide by heating galleïn with aniline and aniline hydrochloride. He describes it as a colorless compound, soluble in alkalies without color, and gives it the formula



$$\begin{array}{l} C_6H_4\text{—}C(C_6H_3OH)_2O_2O \\ \;| \qquad\quad\; | \\ OC\text{———}NC_6H_5 \end{array}$$

From this anilide he made what he calls a dimethyl ether, also colorless, by heating it with methyl iodide in a sealed tube to 100°. Schultz and Julius, in their "Tabellarische Uebersicht der künstlichen organischen Farbstoffe" (edition of 1891, page 98), give galleïn the following formula:



$$C\left\{\begin{array}{l} C_6H_2OH\text{—}O \\ \qquad\quad >O \quad | \\ C_6H_2OH\text{—}O \\ \\ C_6H_4CO\text{—}O \end{array}\right.$$

The same structure is given to it in Léon Lefèvres' "Matières Colorantes Artificielles" (1896, page 1190). Nietzki, in his "Chemie der organischen Farbstoffe" (1897), gives it the structure:

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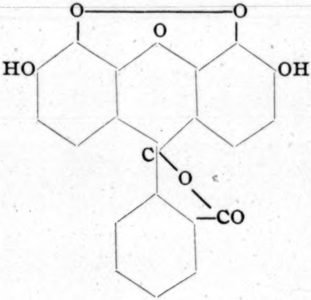
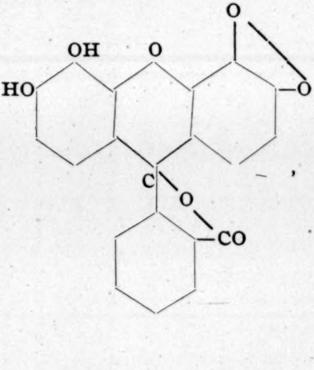
[1] We have adopted the term lactoid instead of lactone. It is more comprehensive and may be used to designate compounds like the anilides and hydrazides of the phthaleïns which are not lactones.

[2] Buletinul Societatii de Sciinte Fizice d. Bucuresci Romania, 1, 215 (1892).

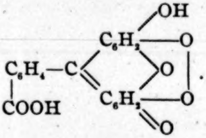
[3] Ber. d. chem. Ges. 26, 3077.



He adds, however: "Wahrscheinlich ist es fast, dass diese beiden Sauerstoffatome in einem Kern eine Orthochinongruppe bilden, auch dürfte das Galleïn zu den chinoïden Carboxylderivaten gehören." Schultz and Julius, in the 1897 edition of their book, page 142, give its structure as follows, representing it as an orthoquinone,



while Krafft in his "Organische Chemie," 1897, page 595, follows the other suggestion of Nietzki and gives it the structure



II. COERULEÏN.

This compound was also discovered by Baeyer[1] in 1871. He made it by heating galleïn with 20 parts of concentrated sulphuric acid to 200° and precipitating the product with water. From the analysis of the substance he deduced the formula $C_{18}H_{10}O_6$ and represented its formation from galleïn by the following equation :

$$\underset{\text{Galleïn.}}{C_{18}H_{14}O_7}—H_2O—H_2=\underset{\text{Coeruleïn.}}{C_{18}H_{10}O_6}.$$

He found that the coeruleïn was reduced to a compound, which he called coerulin, by the action of ammonia and zinc dust. This same coerulin was also obtained from the reduction-product of galleïn, gallin, by gently heating it with concentrated sulphuric acid. In a later paper,[2] after he had determined the correct formula for galleïn to be $C_{20}H_{12}O_7$, he finds that coeruleïn has the formula $C_{20}H_{10}O_7$ and gives the following series :

Gallin, $C_{20}H_{18}O_7$;
Galleïn, $C_{20}H_{12}O_7$;
Coeruleïn, $C_{20}H_{10}O_7$.

Though coeruleïn was the first of the class of compounds, which Baeyer[3] called phthalideïns, to be discovered, its structure was not investigated until after that of phenolphthalideïn had been determined. This phenolphthalideïn was made by the oxidation of phenolphthalidin, resulting from the action of sulphuric acid on phenolphthalin. This phenolphthalidin Baeyer regards as dioxyphenylanthranol, and represents the reaction by which it is formed as follows:

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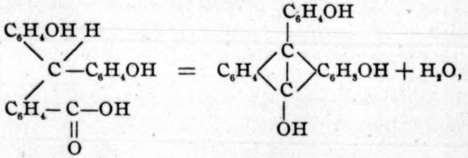
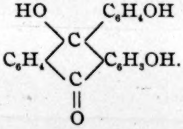
[1] Ber. d. chem. Ges., 4, 556.
[2] *Ibid.*, 4, 663.
[3] Ann. Chem. (Liebig), 202, 90.



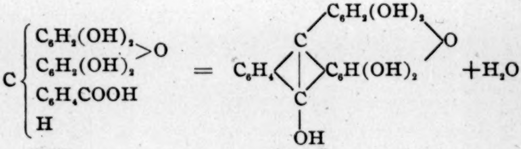
Phenolphthalin. Phenolphthalidin.

since it results from the phthalin by the loss of one molecule of water, and may be converted into the phthalin by superheating with water. Phenolphthalideïn, formed by the oxidation of the phthalidin, he regards as dioxyphenyloxanthranol,



Phenolphthalideïn.

In 1881 Buchka[1] took up the study of coeruleïn and coerulin in connection with his work on galleïn. He found that coerulin is formed from gallin by the action of concentrated sulphuric acid in the same manner as phenolphthalidin from phenolphthalin and represents the reaction by the following equation:



Gallin. Coerulin.

From this coerulin he made what he terms the tetracetyl ether by the action of acetic anhydride. He explains the formation of this compound by assuming that the hydroxyl group, joined to the γ-carbon atom, does not react with acetic anhydride. On oxidation of this coerulin it goes over into coeruleïn, which may also be formed directly from galleïn by heating with concentrated sulphuric acid. Hence, according to Buchka, coeruleïn also contains a quinone group, and if it were analogously constituted to phenolphthalideïn, it would have the formula

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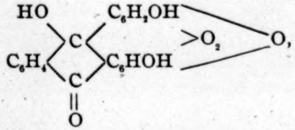
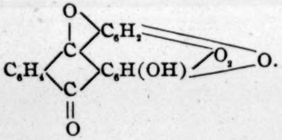
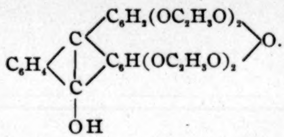
[1] Ann. Chem. (Liebig), 209, 258 and 272.



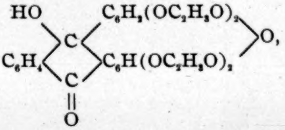
and, on treatment with acetic anhydride, it should give a tetracetyl ether, owing to the reduction of the quinone group; but it gives a red-colored triacetyl ether. In order to explain the formation of this compound, Buchka assumes that the quinone bond in coeruleïn is broken by the action of the acetic anhydride as it is in galleïn, but that the hydroxyl group of the γ-carbon atom then unites with one of the pyrogallol residues with the separation of water and formation of a condition like that in rosolic acid. Thus he arrives at the following formula for coeruleïn :



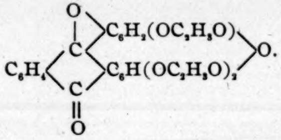
This formula is shown to be correct, he thinks, by the fact that the triacetyl coeruleïn may also be made by the oxidation of the tetracetylcoerulin, which undoubtedly has the formula



This substance could give, on oxidation, a product containing a quinone group by the separation of two acetyl residues, thus forming a diacetyl coeruleïn. It cannot yield, however, a triacetyl ether containing a quinone group. He explains the formation of triacetyl coeruleïn by assuming that the tetracetyl coerulin forms, on oxidation, a tetracetyl coeruleïn, perhaps of this structure,



which, as soon as formed, splits off a molecule of acetic acid and goes over into a triacetyl coeruleïn of the formula



On heating with zinc dust, coeruleïn yields phenylanthracene, according to Buchka, thus showing that it is a derivative of this hydrocarbon.

In 1894 M. Prud'homme[1] published a short article on the constitution of coeruleïn. He states that the substance condenses with 2 molecules of aniline, with the loss of 2 molecules of water, to form a new dye. This new substance does not form lakes with iron, chromium, or aluminium mordants, and hence, he thinks, no longer contains any hydroxyl groups.

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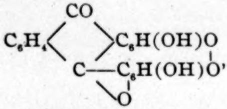
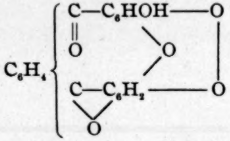
[1] Bull. soc. chim. (Paris), (3), 11, 1136.

The formation of the new compound from coeruleïn depends upon the hydroxyl groups, and as the coeruleïn had the power of combining with 2 molecules of aniline it must contain two hydroxyl groups. This assumption of the presence of two hydroxyl groups in the molecule of coeruleïn is also, according to Prud'homme, in harmony with the law of Liebermann and Kantanecki, that only those oxyketone dyes in which two hydroxyl groups are in the ortho position, act as mordant dyes. He therefore gives the following formula to coeruleïn,

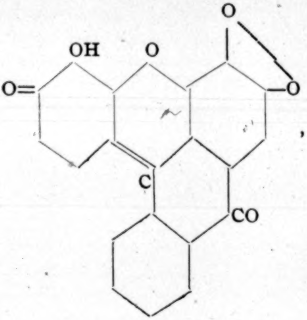


which represents it as containing two hydroxyl groups and as a derivative of phenyloxanthranol.

In Schultz and Julius' "Tabellarische Uebersicht der künstlichen organischen Farbstoffe," edition of 1891, page 98, the following formula is given for coeruleïn:



Nietzki, in his "Chemie der organischen Farbstoffe" (1897), page 175, gives it the same formula, but adds in a foot-note the following remark: "Eine Controlle dieser Formel wäre wohl zeitgemäss. Die vielen Sauerstoffbindungen lassen sich kaum mit den heutigen Anschauungen über derartige ringförmig constituirte Molecule vereinigen. Auch sind die beizenfärbenden Eigenschaften bei Vorhandensein nur einer Hydroxylgruppe kaum zu erklären." In the 1897 edition of their work, page 142, Schultz and Julius give the following formula to coeruleïn,



,

representing it as a quinoid dyestuff containing also an orthoquinone group.

From the foregoing historical review may be gathered the development of ideas in regard to the structure of the phthaleïns and phthalideïns down to the present time. In the following pages is given an account of an investigation undertaken with a view to throwing additional light upon the subject so far as two of these are concerned—galleïn and coeruleïn.

EXPERIMENTAL.

I. GALLEIN.

The galleïn used in this investigation was supplied by the Badische Anilin und Soda Fabrik, Ludwigshafen-am-Rhein, to whom grateful thanks are herewith tendered for the generous interest they have manifested in the work. It was an unusually pure product and beautifully crystallized. By transmitted light it was red; by reflected light, under the microscope, greenish-yellow with a metallic luster. When seen in bulk it has a decided green color. When acetylized it left no residue other than galleïn acetate.

Galleïn dissolves in an aqueous solution of pyrogallol, more easily in boiling solution, from which, after several hours, it crystallizes out. That galleïn, in addition to its marked acid properties, has slight basic properties, is shown by the fact that its solubility in water or alcohol is considerably increased by the presence of an acid. This same conduct on the part of fluoresceïn was noted by Baeyer[1] and by Waddell.[2] In the case of aurin, which resembles galleïn to a marked degree, Dale and Schorlemmer[3] have isolated a hydrochloric acid salt.[4]

When galleïn is dissolved in alcohol and an alcoholic solution of potassium hydroxide in excess is added, the potassium salt of galleïn is precipitated. It has a blue color and probably contains 4 atoms of potassium.

Attempts were made to reduce galleïn by means of hydrogen sulphide. Solutions in ammonium hydroxide, in potassium hydroxide, sodium carbonate, and in alcohol remained unchanged after passing the gas through them for some time. Sulphur dioxide was also tried as a reducing agent, but with negative results. An alcoholic solution of galleïn remains unchanged when treated with sulphur dioxide. Galleïn in dilute caustic potash solution, when treated with sulphur dioxide, is thrown down as a dark-red precipitate, due to the neutralization of the potassium hydroxide.

An aqueous solution of galleïn, made by boiling galleïn with water and filtering the solution, when treated with a solution of lead acetate or lead nitrate in water, gives first a deep-blue solution from which, finally, all the galleïn is precipitated as the basic lead salt, with indigo-blue color. This reaction is quite delicate and might be used as a test for either galleïn or lead. Galleïn does not melt or undergo any change when heated to 300° C.

Air passed through a solution of galleïn in caustic potash solution causes the color to change from deep-blue to brown. Hydrochloric acid added to this brown solution produces vigorous effervescence but no precipitate. It is probable that oxidation takes place here as with pyrogallol itself. This tendency of galleïn to oxidize is seen further in its action on silver nitrate, which it reduces to metallic silver.

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[1] Ann. Chem. (Liebig), **183**, 6.

[2] J. Phys. Chem., **2**, 173.

[3] Ann. Chem. (Liebig), **196**, 88.

[4] Cf. Collie and Tickle on "Salts of Dimethylpyrone and the Quadrivalence of Oxygen." J. Chem. Soc., **75**, 710.

Galleïn Tetracetate.

Galleïn tetracetate was made according to Buchka's directions—by boiling galleïn and an equal weight of sodium acetate in four times the weight of acetic anhydride for four hours. After a number of trials it was found that the acetylization was complete in one hour. The excess of acetic anhydride was distilled off and the residue poured into a large amount of water. The acetate appeared on the bottom of the vessel, partly in the form of crystalline particles, partly as an oil that soon solidified. The product thus obtained was filtered and when dry had a gray color; yield almost quantitative. Crystallized from benzene, it was obtained in colorless needles. Recrystallized from benzene, acetone, alcohol, and acetic acid in succession till no further change in its melting-point could be observed, it was found to melt at 241° C.[1] The melting-point as given by Buchka is 247° to 248°, by Herzig[2] 236° to 237°.

Crystals of galleïn tetracetate and gallin tetracetate, as well as of the so-called hydrogalleïn tetracetate, were examined by Professor A. C. Gill, of the Mineralogical Department of Cornell University, who reports as follows concerning them:

"Galleïn tetracetate crystallizes from a mixture of alcohol and chloroform in bright, transparent, triclinic crystals bounded by the faces c (001), b (010), m (110), M $(1\bar{1}0)$, and x $(10\bar{1})$. The corresponding angles vary considerably on different crystals, permitting only an approximate determination of the crystallographic constants: These are: a : b : c = 0.865 : 1 : 0.626.

$$\alpha = 74^\circ\ 2', \beta = 126^\circ\ 2', \text{ and } \gamma = 99^\circ.$$

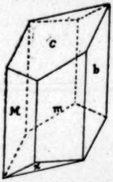
---

[1] All melting-points were determined by means of a thermometer compared with one standardized by the Physikalisch-Technische Reichsanstalt, Charlottenburg, Germany.

[2] Monatsh. Chem., 13, 426.

"The more important anglesa re:

$M : m = 72^\circ\ 4'$;
$m : b = 54^\circ\ 39'$;
$cm : = 69^\circ\ 2'$;
$c : M = 52^\circ\ 12'$;
$c : x = 99^\circ\ 58'$;
$x : m = 47^\circ\ 41'$;
$x : M = 64^\circ\ 21'$.



"On smaller crystals from ether it could be determined that the substance has a large optical angle, is positive, and has a strong dispersion, $v > \rho$. These crystals differ both in habitus and in angles from gallin tetracetate and the so-called hydrogalleïn tetracetate, leaving no doubt that they are a different substance.

"The crystals of gallin tetracetate and of the so-called hydrogalleïn tetracetate, while differing somewhat in habitus, show a similarity of angles in the principal zone, which is, in fact, identical within the limits of error arising from the imperfectness of the crystals. The mean angles were :

"Gallin tetracetate 79°.5, 42°, and 58°.5.

"Hydrogalleïn tetracetate 79°53′, 41°26′, and 58°41′.

Galleïn acetate is insoluble in a cold 5 per cent solution of sodium carbonate ; the solution remains perfectly colorless, though allowed to stand two or three days. When boiled for some time there is partial saponification and a very small part of the acetate dissolves, as shown by the slight pink tinge of the carbonate solution.

When treated with a few drops of concentrated sulphuric acid in the cold, galleïn acetate dissolves, giving the acid solution a deep-red color. When diluted with water the solution retains its red color, and after standing some time deposits red crystals. These crystals, when filtered out and washed with a little water, dissolve in ammonium hydroxide with the purple color and in caustic potash solution with the deep-blue color so characteristic of galleïn, and give also the unmistakable test for galleïn with lead acetate. There can be no doubt that sulphuric acid saponifies the acetate, and the crystals that separate are those of galleïn.

The determination of the exact constitution of galleïn acetate was an urgent matter. The difficulty of deciding it by a combustion-analysis will be seen at once by a comparison of the percentages of carbon and hydrogen in galleïn acetate of different content of acetyl groups.

No. of CH_3CO groups.	C. Per cent.	H. Per cent.	Acetyl groups. Per cent.
4	63.16	3.78	32.34
5	62.72	3.86	37.46
6	62.34	3.92	41.89

From the above it will be seen that the percentage of carbon differs by about 0.4 per cent, hydrogen by about 0.07 per cent in the several cases. Buchka found C = 63.52 and 62.73, H = 4.44 and 3.82, results that agree as well with the assumption that this is a *pent*acetate as that it is a *tetr*acetate.

There is a much wider margin in the percentages of acetyl residues in the three supposed possible formulas, as shown in the last column in the above table. Four C_2H_3O groups would equal 32.34 per cent; five would equal 37.46 per cent, a difference of 5.12 per cent; six would equal 41.89 per cent of the whole molecule, a difference of 4.43 per cent.

Several attempts were made to determine the number of acetyl residues in the acetate by saponification by means of different alkalies, but without success, since the galleïn residue itself undergoes some decomposition when heated with alkalies, giving volatile acid products that have not been further investigated. It was found, however, that a modification of Wenzel's method[1] could be used satisfactorily. The distinguishing points of this method are: First, saponification by means of strong sulphuric acid; second, removal of free sulphuric acid by means of secondary sodium phosphate; third, distillation of the liberated acetic acid *in vacuo*. The three important modifications of the Wenzel method, suggested by this work, are: First, the substitution of distillation in steam for distillation *in vacuo*; second, the abandonment of one of the condensers; third, the use of dimethylamidoazobenzene as an indicator to detect and determine mineral acid in the distillate. The arrangement of the apparatus may be understood from the accompanying sketch: *A* is a 300 cc. distilling flask with delivery tube inclined upwards; *B* is a 100 cc. distilling flask with delivery tube inclined downwards so as to connect easily with *C*, an Allihn condenser. *D* is a 750 cc. Erlenmeyer flask, *F* a small separatory funnel, and *S* a screw-clamp.

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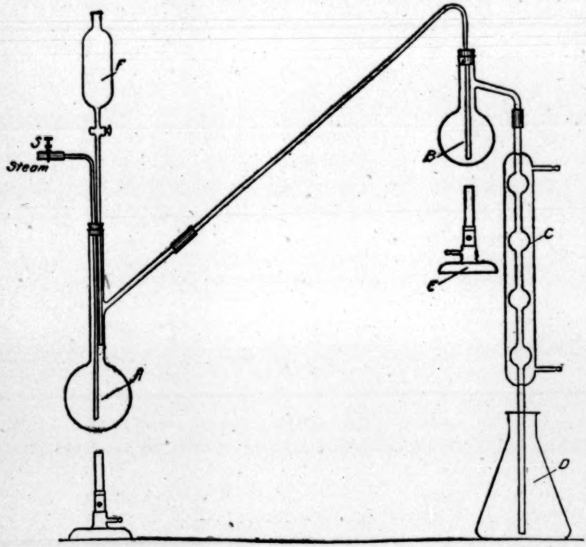
[1] Monatsh. Chem., **18**, 659.



A weighed amount of material is placed in *A* and 3 or 4 cc. of sulphuric acid diluted with water (2 of acid with 1 of water by volume), run in through the funnel *F*, the screw-clamp *S* being closed. An excess of tenth-normal sodium hydroxide solution is measured into flask *D*, the whole apparatus properly connected, and water started through the condenser. The flask *A* is then heated for one hour to the temperature of a boiling water-bath, when 3 cc. of distilled water are added and the heat continued for half an hour longer. There are now introduced 20 cc. of a solution made by dissolving 45 grams of secondary sodium phosphate and 10 grams of glacial phosphoric acid in 100 cc. of water. Finally, add 50 cc. of boiled distilled water, heat with a burner, and pass in steam. Liquid will soon begin to collect in flask *B*, which serves as a trap to prevent acid from being carried over mechanically. When flask *B* is one-fourth full of liquid, heat it with a burner, the heat being so regulated as to keep the liquid at a constant level. When the distillate has collected in the receiver to the amount of 600 cc. stop the heat and transfer the distillate to a liter measuring-flask. Dilute to the mark and mix thoroughly. Measure out 500 cc. of the solution and titrate with tenth-normal hydrochloric acid, using phenolphthaleïn as an indicator. In order to tell whether any mineral acid (H_2SO_3, etc.,) has been carried over, the remaining portion is titrated with tenth-normal hydrochloric acid, using dimethylamidoazobenzene as the indicator. This is sensitive to free mineral acids but not to dilute organic acids. Of course, the amount of mineral acid is to be deducted from the total amount of acid found.

The process of distillation is not yet complete. One or two cc. of tenth-normal sodium hydroxide are again measured into flask *D*, and the heating continued until 300 cc. are collected. This is titrated directly with tenth-normal hydrochloric acid, using phenolphthaleïn as an indicator. The total amount of acid in this distillate is so small as to make the detection of mineral acid impossible—none was discovered in it in any determination made. To make sure that all volatile acid has been driven from flask *A*, a third distillate is collected which rarely showed more than 0.2 cc. tenth-normal sodium hydroxide neutralized. The net amount of tenth-normal sodium hydroxide neutralized, multiplied by 0.0043044 gives the weight of acetyl groups present. This method was used in all the acetyl determinations reported in this paper.

In order to test the apparatus and chemicals, preliminary determinations were made, using a compound of known composition—acetanilide. Two analyses of acetanilide were made by the method given above with the following results :

Weight of substance. Gram.	Tenth-normal sodium hydroxide. cc.	Mineral acid.	Net tenth-normal sodium hydroxide. cc.	C_2H_3O. Per cent.
0.5472	40.25	0.0	40.25	31.66
0.2260	16.85	0.0	16.85	32.09

Calculated percentage of C_2H_3O in acetanilide = 31.84.

Galleïn acetate analyzed according to this method gave the following results :

Weight of substance. Gram.	Tenth-normal sodium hydroxide. cc.	Mineral acid.	Net tenth-normal sodium hydroxide. cc.	C_2H_3O. Per cent.
0.1946	15.1	0.3	14.8	32.74
0.2584	19.7	0.0	19.7	32.82

Calculated[1] for $C_{20}H_7O_7(C_2H_3O)_5$, 37.46 per cent C_2H_3O.
Calculated for $C_{20}H_8O_7(C_2H_3O)_4$, 32.34 per cent C_2H_3O.
Calculated for $C_{20}H_9O_7(C_2H_3O)_3$, 26.33 per cent C_2H_3O.

There can be no doubt from these results that this is a tetracetate of galleïn.

GALLEÏN TETRABENZOATE.

Buchka made this compound by use of benzoyl chloride. It was deemed advisable to try making it from benzoic anhydride. Galleïn (10 grams) and benzoic anhydride (50 grams) were heated to 190° C. on a metal-bath for seven hours. The melt was then transferred to a 2-liter round-bottomed flask and the excess of benzoic anhydride removed with steam. The black residue was filtered out and, after draining thoroughly, dissolved in acetone and boiled with boneblack. The acetone solution was concentrated and a little water added. In a short time yellow crystals appeared which, by repeated crystallization from acetone, alcohol, and acetic acid, became white and melted at 226°. Melting-point given by Buchka is 231°.

Efforts were made to determine the number of benzoyl residues in this compound by the method used in analyzing the acetate, but failed on account of the difficulty of completely saponifying the benzoate by sulphuric acid. But that it contains four benzoyl groups can scarcely be doubted from its analogy to the tetracetate.

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[1] In all calculations in this paper the following atomic weights have been used: O = 16, H = 1.008, C = 12.01, N = 14.04, Ag = 107.92, I = 126.85, S = 32.07, Pb = 206.92.

HYDROGALLEÏN TETRACETATE.

The preparation of this compound from the so-called hydrogalleïn, and its identity with galleïn tetracetate, constitute the basis for Buchka's formula for galleïn. It will be remembered, however, that Herzig tried to make it from Buchka's hydrogalleïn, but did not succeed.

Pure galleïn (made by saponifying the acetate melting at 241°) was dissolved in slight excess of potassium hydroxide solution, zinc dust added cautiously, and the temperature of the contents of the flask prevented from rising by a stream of cold water around the flask. When the blue color of the alkaline solution disappeared, becoming more or less brown, dilute sulphuric acid was added slowly and in such a way as to prevent an appreciable rise in temperature. The acid liquid was extracted with ether, the ether solution rapidly filtered to remove suspended particles, and dried over calcium chloride in an atmosphere of carbon dioxide. The ether solution was then distilled in a stream of carbon dioxide. An oil with a slight red color remained and on standing solidified. Acetic anhydride in excess was added and the liquid boiled on a metal-bath, for four hours, in a flask connected with a reflux condenser. A portion of the excess of acetic anhydride was distilled off and the residue poured into water. The acetate collected on the bottom of the vessel as an oil, which afterwards solidified. The yellow substance was crystallized from benzene, and gave a product melting at 213°–214°. It was recrystallized from alcohol and acetic acid in succession till the melting-point was constant. The final product was colorless and melted at 216°.

These crystals were examined by Dr. Gill, of the Mineralogical Department of the University, and compared with crystals of gallin tetracetate. The crystals of both were found to be triclinic and the angle measurements in the principal zones were the same within the limits of error. In all probability, therefore, the hydrogalleïn and gallin tetracetates are crystallographically identical.

The difference between hydrogalleïn and galleïn acetate is seen in their conduct with sodium carbonate and concentrated sulphuric acid. The former, when treated with a five per cent solution of sodium carbonate in the cold, dissolves at once, imparting to the solution at first a greenish-yellow fluorescence; the color rapidly deepens, becoming later a decided purple, owing to saponification and oxidation. The hydrogalleïn acetate, when treated with a few drops of cold concentrated sulphuric acid, dissolves with a red color. When this solution is diluted with water it forms a green solution which, after standing, deposits a green precipitate. This, filtered off and washed with a little water, dissolves in ammonium hydroxide with the green color and in aniline with the blue color, both characteristic of coeruleïn. Sulphuric acid saponifies the so-called hydrogalleïn acetate and condenses one of the products (gallin) even in the cold to coerulin, which is easily oxidized in alkaline solution to coeruleïn, forming a green solution with ammonium hydroxide, and dissolving in aniline with a blue color.

Analyses for the purpose of determining the number of acetyl groups in this compound gave the following results:

Weight of substance. Gram.	Tenth-normal sodium hydroxide. cc.	Mineral acid. cc.	Net tenth-normal sodium hydroxide. cc.	C_2H_3O. Per cent.
0.2328	21.5	4.0	17.5	32.36
0.1690	15.7	2.75	12.95	32.98

Calculated for $C_{20}H_{11}O_7(C_2H_3O)_3$, 26.22 per cent C_2H_3O.
Calculated for $C_{20}H_{10}O_7(C_2H_3O)_4$, 32.21 per cent C_2H_3O.
Calculated for $C_{20}H_9O_7(C_2H_3O)_5$, 37.33 per cent C_2H_3O.

Clearly the compound is a tetracetate, but it has none of the characteristics of galleïn tetracetate but all the properties of gallin tetracetate described below.

We repeated this experiment a great number of times, following Buchka's directions to the letter but always with the same result. The product was absolutely identical in every respect with gallin tetracetate. We must hence conclude that hydrogalleïn and its acetate do not exist.

GALLIN TETRACETATE.

This compound was made by the method given by Buchka. Galleïn, dissolved in ammonium hydroxide, was reduced to gallin by means of zinc dust, the solution being kept at the boiling-point. After boiling thus for two hours, the purple color having disappeared, dilute sulphuric acid was added little by little through the condenser-tube till in slight excess. The acid solution was filtered while hot and cooled in an atmosphere of carbon dioxide. It was then shaken with ether to dissolve the gallin, the ether solution separated and filtered, dried over calcium chloride in an atmosphere of carbon dioxide, and finally the ether distilled off in a current of carbon dioxide. The residue, gallin, appeared as a red oil which solidified on standing. This was converted into the acetate in accordance with the directions given under hydrogalleïn tetracetate. The crude material was recrystallized from alcohol and acetic acid and gave a colorless product melting at 216° C. Its conduct with a five per cent solution of sodium carbonate and with concentrated sulphuric acid was identical with that of the so-called hydrogalleïn acetate described above.

The difficulty of deciding the composition of gallin acetate by combustion-analysis will appear from the following table, which gives the percentages of carbon and hydrogen according to the different formulas:

No. of acetyl groups.	C. Per cent.	H. Per cent.
3	63.41	4.09
4	62.92	4.15
5	62.50	4.20

Buchka found C = 62.72 per cent; H = 4.37 per cent.

Determinations of the number of acetyl groups in gallin acetate resulted as follows:

Weight of substance. Gram.	Tenth-normal sodium hydroxide. cc.	Mineral acid. cc.	Net tenth-normal sodium hydroxide. cc.	C_2H_3O Per cent.
0.2490	20.3	1.5	18.8	32.50
0.1728	14.4	1.2	13.2	32.88

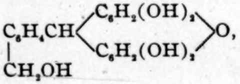
Calculated for $C_{20}H_{11}O_7(C_2H_3O)_3$, 26.22 per cent C_2H_3O.
Calculated for $C_{20}H_{10}O_7(C_2H_3O)_4$, 32.21 per cent C_2H_3O.
Calculated for $C_{20}H_9O_7(C_2H_3O)_5$, 37.33 per cent C_2H_3O.

In view of these results this compound is correctly called gallin tetracetate.

The residue in flask *A* (see sketch), when treated with an excess of caustic potash, gives a blue color, as would be expected of gallin in presence of air.

GALLOL ACETATE.

Buchka claims to have obtained a lower reduction-product of galleïn by the use of zinc dust and acid solution. Having the formula as given by him,



$$\begin{array}{l} C_6H_4CH\left\langle\begin{array}{l}C_6H_2(OH)_2\\ C_6H_2(OH)_2\end{array}\right\rangle O, \\ | \\ CH_2OH \end{array}$$

gallol would be expected to yield a pentacetate. According to Buchka's method for making this substance, galleïn (5 grams) was placed in a liter flask with 700 cc. of water, a little dilute sulphuric acid added, and some zinc dust. The solution was kept boiling for ten hours, small amounts of dilute acid and zinc dust being added from time to time. The solution lost its deep-red color and became straw-yellow. It was then filtered and allowed to cool. A small deposit of crystals appeared after awhile on the bottom of the vessel. The solution was shaken with ether and the ether dried and distilled off with the same precautions as noted under hydrogalleïn tetracetate. A residue was left as a red oil, to which were added the crystals which had separated, and the whole acetylized. The acetate was recrystallized from alcohol, yielding colorless crystals melting sharply at 216°. Buchka's gallol pentacetate melted at 230°.

The product made as above described reacted with a 5 per cent solution of sodium carbonate and with concentrated sulphuric acid in every respect as the gallin tetracetate and could not be distinguished from it in any way. A determination of the number of acetyl groups resulted thus :

Weight of substance. Gram.	Tenth-normal sodium hydroxide. cc.	Mineral acid. cc.	Net tenth-normal sodium hydroxide. cc.	C_2H_3O. Per cent.
0.2237	20.5	3.46	17.04	32.79

Calculated for $C_{20}H_{10}O_7(C_2H_3O)_4$, 32.21 per cent C_2H_3O.

A pentacetate, according to Buchka's formula, would have 38.26 per cent C_2H_3O. This substance, therefore, not only shows all the characteristics of gallin tetracetate but the results obtained on analysis prove the identity of the two products.

An attempt was made to reduce galleïn in acetic acid solution to gallol by the action of sodium amalgam, with negative results. Only gallin tetracetate could be isolated.

An effort was made to prepare gallol acetate directly from galleïn acetate. Galleïn (5 grams) was mixed with an equal weight of sodium acetate and 25 grams acetic anhydride and boiled in a flask connected with a return-condenser for one hour. Zinc dust in small amounts was added from time to time, while the boiling was continued for three hours. A small quantity of the material was taken out, the acetate formed crystallized once from alcohol and found to melt at 215°, and to dissolve in dilute ammonia with a purple color. The remainder of the mixture was boiled seven hours longer, zinc dust in small quantities being added from time to time. The product crystallized once from alcohol, melted at 214°.5, and dissolved in dilute ammonia with a purple color. Thus it would appear to be impossible to obtain gallol by reduction of galleïn or its acetate with zinc dust in acid solution, even on prolonged heating.

METHOD FOR THE PREPARATION OF GALLIN TETRACETATE.

As a result of this work, however, a method for the preparation of gallin acetate was found which is very much shorter and simpler than that described by Buchka, and gives a yield almost as great as that required by theory. To 5 grams of galleïn add 5 grams of fused sodium acetate and 20 cc. of acetic anhydride. Boil in a flask connected with a return-condenser for fifteen minutes, add 2 grams zinc dust, and boil fifteen minutes longer. Allow the excess of zinc dust to settle to the bottom of the flask and pour off the solution carefully into a half liter of water. A small portion of the precipitate is granular; the bulk of it is an oil which soon solidifies, especially when agitated. Recrystallize from acetic acid (40 per cent), using boneblack to decolorize, afterwards from alcohol slightly diluted with water.

SILVER SALT OF GALLIN TETRACETATE.

That gallin tetracetate is an acid was shown not only by its dissolving in dilute sodium carbonate solution but also by making its silver salt. Gallin acetate was dissolved in 95 per cent alcohol and an alcoholic solution of silver nitrate added in excess. The mixture was heated to boiling, filtered, and left in the dark for several hours. There separated a white precipitate resembling, in appearance, silver chloride. It was practically insoluble in alcohol when once precipitated, did not melt sharply, but decomposed when heated, and turned dark when exposed to sunlight.

The so-called gallol acetate gave rise to the same compound under the same conditions—another proof of the identity of gallin and gallol acetates.

On analysis the compound gave the following results for silver.

	Weight of substance. Gram.	Weight of silver. Gram.	Silver. Per cent.
I	0.1044	0.0172	16.48
II	0.1072	0.0179	16.70

Calculated for $C_{20}H_9O_7(CH_3CO)_4Ag$, 16.83 per cent Ag.

The analysis was made by placing the well-washed and dried product in a small porcelain crucible and burning out the organic matter by careful ignition.

The first analysis above was made from a product obtained from the so-called gallol acetate, the second from gallin acetate.

GALLEÏN METHYL ESTER.

This compound was made by one of the usual methods for the preparation of esters. Galleïn (5 grams), methyl alcohol

(30 cc.), and concentrated sulphuric acid (10 cc.) were mixed, forming a deep-red solution. This was boiled in a flask connected with a return-condenser for one and one-quarter hours, when there separated a good quantity of crystals. The mass was then poured into 500 cc. water, filtered, the residue washed and dried, at first in the air, finally in an air-bath at 70°. To free the ester from any galleïn which might have been present, the ester was dissolved in ether, in which galleïn is insoluble, the solution filtered and concentrated. The ester came down in granular masses of dark red color, with bronzy luster. It dissolves in alcohol, acetone, ether, chloroform, acetic ether with red color, but is almost insoluble in benzene. It dissolves at once in alkalies and alkaline carbonates with the colors characteristic of free galleïn in these solvents—probably owing to saponification. It did not melt when heated to 280° C.

A determination of the methoxy group by Zeisel's method in a sample dried at 100° C. resulted as follows:

Weight of ester. Gram.	Weight of silver iodide. Gram.	CH_3O. Per cent.
0.1819	0.1011	7.34

Calculated for $C_{19}H_8O_2(OH)_3COOCH_3$, 8.20 per cent.

GALLEÏN ETHYL ESTER.

Galleïn (5 grams), absolute alcohol (30 cc.), and concentrated sulphuric acid (20 cc.) were heated in a flask provided with a return-condenser for two and three-quarters hours. The galleïn was entirely in solution at the beginning of the operation and, while still heating, crystals in good quantity were deposited. The mixture was poured into 500 cc. water, filtered, and washed. The ester appeared as beautiful crystals, red by transmitted light, green by reflected light. It dissolves in alcohol, acetone, ether, chloroform, and acetic ether with red color. Quite a number of efforts were made to crystallize it from different solvents, but the best method of purifying it was found to be solution in anhydrous ether, filtering to remove galleïn, and concentration of the solution almost to dryness. The ester then appeared as granular masses.

Analysis of a sample dried at 100° C. to constant weight gave, by Zeisel's method, the following result :

Weight of ester. Gram.	Weight of silver iodide. Gram.	C_2H_5O. Per cent.
0.0811	0.0518	12.25

Calculated for $C_{19}H_8O_2(OH)_3COOC_2H_5$, 11.48 per cent.

The results obtained with the methyl and the ethyl esters of galleïn indicate very clearly that galleïn is an acid and contains one carboxyl group. It is probable that what Baeyer considered alcohol of crystallization was in reality due to the presence of this ester.

GALLEÏN TRIPHENYLCARBAMATE.

By the action of phenyl isocyanate upon galleïn, combination took place, giving rise to a new compound. Galleïn dried at 100° C., and a little more than the calculated amount of phenyl isocyanate, were heated quickly to the boiling-point of the mixture and kept at this temperature for ten minutes—agitating from time to time. On cooling, the residue appeared as a black tar. This was taken up in benzene, the solution filtered, boiled with boneblack, and allowed to stand. A small amount of a crystalline deposit appeared which was filtered out and found to consist largely of diphenyl urea. To the filtrate petroleum ether was added, when there appeared a bulky yellow precipitate. This was filtered out and dissolved in a little chloroform. On standing, some white crystals appeared which did not saponify with caustic potash solution, and melted at 235° C., and were probably diphenyl urea. This was removed by filtration and the galleïn phenylcarbamate precipitated from the chloroform solution by petroleum ether, filtered out, and the process of dissolving in chloroform and precipitating with petroleum ether continued till no further signs of diphenyl urea appeared.

The galleïn carbamate thus made is a solid, with a light yellow color. It does not melt sharply on account of decomposition and dissolves in alcohol and acetone with green fluorescence. It is an acid, as is shown by the fact that it is soluble in cold dilute sodium carbonate solution with purple color, which is changed to red by acids. The red color of the acid solution is not changed to purple by ammonia solution as would be the case were galleïn formed here. The carbamate dissolves also in a cold dilute solution of ammonia with color, green by reflected light, red by transmitted light. In caustic alkali it dissolves (apparently with saponification) giving a deep-blue solution.

The nitrogen in this compound was determined by Dafert's modification of the Kjeldahl method. A weighed amount of carbamate was placed in a 300 cc. digesting flask, 10 cc. of alcohol added to dissolve it, 30 cc. dilute sulphuric acid (1 : 5) added, and a small amount of zinc dust. The mixture was heated in a flask fitted with a return-condenser till the color nearly disappeared. The flask was then disconnected from the condenser, and the alcohol and water evaporated till the organic matter first showed signs of charring. The remainder of the process was that of the Gunning modification of the ordinary Kjeldahl method. The following results were obtained :

	Weight of carbamate.	Tenth-normal ammonia.	Amount of nitrogen.	
	Gram.	cc.	Gram.	Per cent.
1	0.4274	18.0	0.025272	5.91
2	0.2711	11.4	0.0160056	5.90
3	0.1966	7.8	0.0109512	5.57
4	0.2116	8.3	0.0116532	5.51
5	0.2204	8.7	0.0122148	5.54
6	0.2372	9.35	0.0131274	5.53

Calculated for $C_{20}H_9O_7(OCNHC_6H_5)_3$, 5.83 per cent N.

Calculated for $C_{20}H_8O_7(OCNHC_6H_5)_4$, 6.68 per cent N.

Calculated for $C_{20}H_8O_7(OCNHC_6H_5)_2$, 4.67 per cent N (the formula for this compound on the basis of Buchka's formula for galleïn).

The analyses above recorded were made from two samples which were prepared at different times—1 and 2 from one, 3, 4, 5, and 6 from the other. The results can lead to but one conclusion, that there are three phenyl isocyanate residues introduced and that the compound is galleïn triphenylcarbamate.

GALLEÏN BASIC LEAD SALT.

A sodium carbonate solution was boiled with an excess of galleïn till there was no further evolution of gas. This solution was then filtered from the excess of galleïn and an excess of lead acetate solution added. The precipitate was filtered out and washed till the wash-water no longer gave a test for lead, and dried at 120° C. The lead compound was a dark-blue powder. On analysis for lead the following results were found :

Weight of substance. Gram.	Weight of Lead sulphate. Gram.	Lead. Per cent.
0.9343	0.8960	65.49
0.1975	0.1880	65.0

Calculated for $C_{20}H_8O_7(PbOH)_4$, 65.90 per cent Pb.

GALLEÏN TRIMETHYL ETHER.

Five grams of galleïn were dissolved in 200 cc. of methyl alcohol, 4 grams of caustic potash in 50 cc. methyl alcohol, the two solutions united, and a portion (100 cc.) of the solvent distilled off. To the residue was added methyl iodide (15 grams), and the whole heated to boiling on a water-bath for twenty to thirty hours. At intervals of about eight hours, 1 or 2 grams of solid caustic potash were added, heated for one hour, and about 5 grams methyl iodide added. The solution, at first blue, quickly becomes red. After sufficient heating, the methyl alcohol and excess of methyl iodide were distilled off on a water-bath, the residue treated with 500 cc. of a one per cent solution of potassium hydroxide to dissolve any partially methylated products, and filtered. The insoluble residue will be considered in connection with the tetramethyl ethers.

The alkaline filtrate was acidified with a little concentrated hydrochloric acid. A yellow precipitate was thrown down which was filtered out and washed. The dried residue was dissolved in acetone, boiled with boneblack, concentrated, a little water added, and allowed to stand. After a few hours there was a good yield of crystals which had a golden-yellow color. These were then dissolved in alcohol, boiled with boneblack, concentrated, and allowed to crystallize—a little water being added. Additional crops of crystals were obtained by further dilution of the mother-liquors. By repetition of this treatment crystals were finally obtained which were colorless and melted at 229°.

Determinations of the number of methoxy groups present were made by Zeisel's method. Apparatus and chemicals were first tested by making a determination of the methoxy group in anisic acid, with the following result :

Weight of anisic acid. Gram.	Weight of silver iodide. Gram.	CH_3O. Per cent.
0.1905	0.2910	20.19

Calculated for $C_6H_4(OCH_3)COOH$, 20.39 per cent CH_3O.

The following results were obtained with the galleïn methyl ether dried at 100° C. :

Weight of ether. Gram.	Weight of silver iodide. Gram.	CH_3O. Per cent.
0.1866	0.3100	21.96
0.2376	0.3966	22.06

Calculated for $C_{20}H_8O_5(OCH_3)_2$ according to Buchka's formula),[1] 15.90 per cent CH_3O.

Calculated for $C_{20}H_9O_4(OCH_3)_3$, 22.91 per cent CH_3O.

Calculated for $C_{20}H_8O_3(OCH_3)_4$, 29.53 per cent CH_3O.

The substance is hence a trimethyl ether.

The best method for making the galleïn trimethyl ether in excess is as follows : The galleïn (1 molecule) is dissolved in methyl alcohol in the proportions given above, the calculated amount of caustic potash (4 molecules), also dissolved in methyl alcohol, is added, and from one-third to one-half of the alcohol is distilled off on the water-bath. An excess of methyl iodide is then added, the flask connected with a reflux-condenser, and the mixture is kept gently boiling on the water-bath for ten hours. The alcohol and excess of methyl iodide are then distilled off on the water-bath, and the dry residue treated with a one per cent solution of caustic potash. The rest of the treatment is as given above. Repeated additions of caustic potash and methyl iodide and longer heating increase the yield of the galleïn tetramethyl ether.

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[1] The solubility of this ether in alkaline solutions is a further argument against the correctness of Buchka's formula for galleïn.

Some of the galleïn trimethyl ether recrystallized from ether was examined by Dr. Gill. The crystals were found to be triclinic. The dispersion was strong, $v>\rho$. The optical angle was large and the crystals were optically positive.

Galleïn trimethyl ether dissolves in alcohol and acetone with a delicate pink tint; in benzene its solution is colorless. It resembles phenolphthaleïn quite closely. In dilute sodium carbonate solution, in dilute ammonia, as well as in caustic alkalies, it dissolves at once, even in the cold, with a deep-red color. From such solutions, by the addition of acids, it is precipitated again as the colorless trimethyl ether.

This galleïn trimethyl ether was also made by saponification of the colored tetramethyl ether as stated below.

TRIMETHYL GALLEÏN MONACETATE.

Galleïn trimethyl ether was mixed with an equal weight of fused sodium acetate and five times its weight of acetic anhydride, and the mixture kept at the boiling-point for one hour. The excess of acetic anhydride was distilled off and the residue poured into a large bulk of water. The precipitate was at first oily, but soon solidified. This was filtered off and washed. The residue thus obtained was recrystallized from alcohol. The crystals were needle-shaped and colorless, showed double refraction, and were either monoclinic or triclinic. Melting-point 197°. They dissolve in alcohol, acetone and chloroform, are insoluble in cold aqueous caustic potash, but after prolonged boiling they dissolve, giving a red color to the solution (apparently after saponification of the acetyl group). Saponification takes place more readily in alcoholic caustic potash.

The product dried at 100° C. and analyzed for methoxy groups gave the following results:

Weight of substance. Gram.	Weight of silver iodide. Gram.	CH_3O. Per cent.
0.2004	0.3028	19.97
0.1690	0.2570	20.10

Calculated for $C_{20}H_8O_4(OCH_3)_3(C_2H_3O)$, 20.76 per cent CH_3O.

The results of these analyses show that this derivative of galleïn contains three methoxy groups and one acetyl group. Its properties also harmonize with this view.

GALLEÏN TETRAMETHYL ETHER—COLORED.

The residue insoluble in alkalies, obtained in making the trimethyl ether of galleïn, was dissolved in 50 per cent alcohol, boiled with a little boneblack to remove gummy material, concentrated, and allowed to crystallize. Two distinct sets of crystals were deposited. One set consisted of pyramidal crystals belonging to the monoclinic system. They were red, the larger ones exhibiting a bronzy luster. By far the larger proportion of the crystals was of this sort. The others were much lighter in color and were needle-shaped. These latter will be discussed under the head of galleïn tetramethyl ether —colorless.

The dark-red crystals, mentioned above, melt sharply at 199°, dissolve in alcohol, acetone, chloroform, ether, and acetic ether, with red color. The ether is insoluble in cold alkalies; in hot alkalies it forms a red solution—after saponification. To an alcoholic solution of the ether a solution of sodium carbonate was added, the solution evaporated to dryness on a steam-bath, the residue dissolved in water and filtered, the filtrate acidified, when there appeared a precipitate with a yellow color. This was filtered out, recrystallized from alcohol, and found to be colorless and to melt at 229°. The product showed also all the other characteristics of the galleïn trimethyl ether already described. The number of methoxy groups in the colored methyl ether was determined with the following results:

Weight of substance. Gram.	Weight of silver iodide. Gram.	CH_3O. Per cent.
0.1770	0.3828	28.59
0.2140	0.4656	28.76

Calculated for $C_{20}H_8O_3(OCH_3)_4$, 29.53 per cent CH_3O.
Calculated for $C_{20}H_9O_4(OCH_3)_3$, 22.91 per cent CH_3O.

This ether is unquestionably a galleïn tetramethyl ether, and since one of the methyl groups may be split off by the action of sodium carbonate solution, leaving a product with three methyl groups (see galleïn trimethyl ether above), one of the methyl groups must replace a hydrogen atom of a carboxyl group; *i. e.*, the substance is a monomethyl ester of trimethyl galleïn.

GALLEÏN TETRAMETHYL ETHER—COLORLESS.

The light-colored, needle-shaped crystals referred to above were separated from the deep-red ones, dissolved in acetic acid, boiled with boneblack, and filtered. The slightly red solution was diluted with water till a precipitate appeared, then heated till all dissolved, and allowed to cool slowly. The crystals which separated still had some color. To remove this they were dissolved in alcohol, a little potassium hydroxide was added, and the solution heated to boiling. This saponified the colored ether, forming the potassium salt of the trimethyl ether, which is easily soluble in water. The alcoholic solution diluted with water yields colorless crystals of the tetramethyl ether. These are needle-shaped, show double refraction, and are either monoclinic or triclinic.

The same compound was obtained by heating galleïn trimethyl ether with an excess of methyl iodide in a sealed tube to 125° C. for five hours.

The colorless ether melts at 195°, is soluble in alcohol, acetone, and chloroform, but to a less degree than the colored ether. It is insoluble in aqueous caustic potash (laboratory reagent) even on boiling.

Analysis of a sample dried at 100° C. gave the following results:

Weight of substance. Gram.	Weight of silver iodide. Gram.	CH_3O. Per cent.
0.0804	0.1751	28.77

Calculated for $C_{20}H_8O_3(OCH_3)_4$, 29.53 per cent CH_3O.

GALLEÏN TETRAETHYL ETHER—COLORED.

Galleïn (5 grams) was dissolved in 200 cc. of methyl alcohol,[1] caustic potash (4 grams) in 50 cc. of the same solvent and the two united. A portion (100 cc.) of the solvent was distilled off, and to the residue was added an excess of ethyl iodide. The color changes from blue to red. The mixture was kept at the boiling-point for from five to ten hours. The methyl alcohol and the excess of ethyl iodide were then distilled off on a water-bath. The residue was treated with 500 cc. of a one per cent solution of potassium hydroxide to dissolve any partially ethylated products, and filtered. From the filtrate was separated the triethyl ether as described below.

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[1] Methyl alcohol was used in this case because it is a better solvent than ethyl alcohol for the potassium salt of galleïn.

The residue insoluble in alkali was a deep red viscous mass, which slowly hardened. This was dissolved in methyl alcohol, boiled two or three times with boneblack to remove gummy impurities, concentrated, and allowed to stand several days. There appeared first needle-shaped crystals, which were filtered out and are described below as the colorless tetraethyl ether. After these, in greater amount, came tabular, monoclinic crystals of a deep-red color, which melted at 155°, and whose corresponding angles were the same as those of the colored tetramethyl ether. This ether dissolves in methyl alcohol, ethyl alcohol, acetone, chloroform, acetic ether, and acetic acid. In cold alkalies it is insoluble. If some of the ether is dissolved in alcohol, a little sodium carbonate or potassium hydroxide added, and the mixture heated to dryness on a water-bath, it undergoes saponification. This was shown by dissolving the residue in water, filtering, acidifying the filtrate, when a yellow precipitate was thrown down. This product, on recrystallization, proved to be colorless, and showed the characteristic properties of the triethyl ether described below.

The following are the results of determinations of the ethoxy groups:

Weight of substance. Gram.	Weight of silver iodide. Gram.	C_2H_5O. Per cent.
0.2015	0 3788	36.08
0.1199	0.2356	37.71

Calculated for $C_{20}H_8O_3(OC_2H_5)_4$, 37.82 per cent C_2H_5O.
Calculated for $C_{20}H_9O_4(OC_2H_5)_3$, 30.14 per cent C_2H_5O.

From the above analyses, as well as from the method of its preparation and its properties and reactions, this ether is the analogue of the colored galleïn tetramethyl ether.

GALLEÏN TETRAETHYL ETHER—COLORLESS.

The needle-shaped crystals referred to in connection with the colored tetraethyl ether after recrystallization from alcohol, using boneblack to decolorize, were obtained almost colorless, and found to melt at 144°. They dissolve in alcohol, acetone, acetic acid, and chloroform, but less easily than the colored variety. This ether is insoluble in aqueous alkalies, even on boiling. Analysis gave the following result for the ethoxy group :

Weight of ether. Gram.	Weight of silver iodide. Gram.	C_2H_5O. Per cent.
0.0682	0.1301	36.61

Calculated for $C_{20}H_8O_3(OC_2H_5)_4$, 37.82 per cent C_2H_5O.

GALLEÏN TRIETHYL ETHER.

The alkaline filtrate obtained in the preparation of galleïn tetraethyl ether was acidified with concentrated hydrochloric acid. A heavy yellow precipitate was thrown down. This was filtered out, washed well, and recrystallized from alcohol, using boneblack to decolorize. Colorless crystals were obtained which, on analysis, gave the following result:

Weight of substance. Gram.	Weight of silver iodide. Gram.	C_2H_5O. Per cent.
0.1057	0.1765	32.04

Calculated for $C_{20}H_9O_4(OC_2H_5)_3$, 30.14 per cent C_2H_5O.
Calculated for $C_{20}H_8O_3(OC_2H_5)_4$, 37.82 per cent C_2H_5O.

Galleïn triethyl ether dissolves easily in most of the organic solvents. In cold dilute sodium carbonate solution, in dilute ammonia, as well as in the caustic alkalies, it dissolves at once with deep-red color, just as phenolphthaleïn does. On acidifying these solutions the colorless triethyl ether is reprecipitated.

GALLIN PENTAMETHYL ETHER.

Galleïn was reduced by zinc dust in alkaline solution, and, after acidifying, the resulting gallin extracted with ether in the usual way. After complete removal of the ether by distillation in carbon dioxide, the flask containing the residue was connected with a return-condenser and also a hydrogen generator. After removing as completely as possible all air from the apparatus by means of hydrogen, a slight excess of potassium hydroxide dissolved in 95 per cent alcohol was added through the condenser-tube. The solution turned light-blue due to slight oxidation. After heating five minutes an excess of methyl iodide was added and the mixture heated to boiling on a water-bath for ten hours. The alcohol and excess of methyl iodide were distilled off and the residue treated with 500 cc. of a one per cent solution of caustic potash. The residue was filtered out, washed, and recrystallized from alcohol, using boneblack to decolorize. The crystals at first were more or less yellow; recrystallized from alcohol and acetic acid in succession they became almost white and melted at 127°.

Analyses gave the following results:

Weight of substance. Gram.	Weight of silver iodide. Gram.	CH_3O. Per cent.
0.1596	0.4167	34.51
0.1877	0.4887	34.42

Calculated for $C_{20}H_9O_2(OCH_3)_5$, 35.55 per cent CH_3O.

Calculated for $C_{20}H_{10}O_3(OCH_3)_4$, 29.38 per cent CH_3O.

The compound is therefore the pentamethyl ether of gallin.

The ether dissolves readily in alcohol, acetone, and acetic acid. It is insoluble in cold alkalies, but may be saponified by the method already outlined in connection with the colored galleïn tetralkyl ethers, giving a product that is colorless and dissolves in alkalies without color.

II. COERULEÏN.

The coeruleïn used for the following investigation was also furnished by the Badische Anilin und Soda Fabrik, and was of exceptional purity.

It was found that if coeruleïn is pulverized and suspended in water, it can be dissolved by saturating the water with sulphur dioxide. This filtered solution, when boiled for some time to remove the gas, was decomposed and coeruleïn precipitated. When filtered out and dried, it had a beautiful bronzy luster and seemed to be crystallized.

One marked difference between galleïn and coeruleïn is that while the former dissolves easily in a solution of sodium carbonate the latter is practically insoluble in such a solution, imparting to it only a faint yellow color even after boiling for some time.

In aniline, pyridine, and quinoline, coeruleïn dissolves, more readily if heated. In aniline it forms a deep-blue solution, the color remaining unchanged in excess of acetic acid. The solution in pyridine is colored greenish-blue, which turns purple in excess of acetic acid. On boiling with quinoline the color is purple, which becomes greenish-blue on cooling, and green when diluted with more quinoline.

COERULEÏN TRIACETATE.

Coeruleïn acetate was made according to the method given by Buchka—by boiling coeruleïn with sodium acetate and excess of acetic anhydride. After completion of the reaction a part of the acetic anhydride was distilled off and the residue poured into water. The red precipitate was filtered out and washed. Unsuccessful attempts were made to crystallize the acetate from glacial acetic acid, alcohol, acetone, chloroform, benzene, and acetic ether, in each of which it dissolves with red color. It was finally purified by dissolving it in acetone, filtering, evaporating to small bulk, and precipitating the acetate by adding to the acetone solution a saturated solution of sodium chloride. After washing till the filtrate gave no reaction for chlorides and drying, coeruleïn acetate appeared as a reddish-brown powder.

That it is coeruleïn triacetate cannot be doubted from the following determinations of the number of acetyl groups present:

Weight of acetate. Gram.	Tenth-normal sodium hydroxide. cc.	Mineral acid. cc.	Net tenth-normal sodium hydroxide. cc.	C_2H_3O. Per cent.
0.2153	16.79	2.55	14.24	28.47
0.1753	13.50	2.05	11.45	28.12

Calculated for $C_{20}H_7O_6(C_2H_3O)_3$, 27.33 per cent C_2H_3O.
Calculated for $C_{20}H_6O_6(C_2H_3O)_4$, 33.47 per cent C_2H_3O.

The difficulty of deciding by combustion analysis how many acetyl groups this compound contains will be seen from the following table :

No. of acetyl groups.	Per cent C.	Per cent H.
3	66.10	3.41
4	65.37	3.53

Buchka found C = 65.7 and 66.71, and H = 3.75, but nevertheless calls the compound the triacetate.

COERULIN PENTACETATE.

Buchka's directions were followed in the preparation of this compound, using 5 grams of coeruleïn, 25 grams of acetic anhydride, and a little zinc dust. After heating for twenty minutes the mass began to solidify and had a dark-green color. The contents of the flask were transferred to a porcelain evaporator and heated on the water-bath till nearly all the acetic anhydride disappeared. The residue was then put into 1200 cc. of water to remove all zinc salts, etc., filtered, and washed. The mass was dark-green. Recrystallized from glacial acetic acid, the acetate appears in greenish-yellow needles, which show parallel extinction and form a felted mass. Solutions of coerulin acetate in acetic acid, alcohol, acetone, and chloroform have a greenish-yellow fluorescence. Buchka gives the melting-point of this compound as 256° C. This could not be verified—the compound decomposed when heated and did not melt at all.

Determinations of the number of acetyl groups in this compound resulted as follows :

Weight of acetate. Gram.	Tenth-normal sodium hydroxide. cc.	Mineral acid. cc.	Net tenth-normal sodium hydroxide. cc.	C_2H_3O. Per cent.
0.1837	19.9	3.05	16.85	39.48
0.1991	20.55	2.25	18.3	39.56

Calculated for $C_{20}H_8O_6(C_2H_3O)_4$, 33.34 per cent C_2H_3O.

Calculated for $C_{20}H_7O_6(C_2H_3O)_5$, 38.54 per cent C_2H_3O.

The product is therefore a pentacetate.

Calculated percentages of carbon and hydrogen are as follows :

No. of C_2H_3O groups.	Per cent C.	Per cent H.
4	65.11	3.90
5	64.51	3.97

Buchka found C = 65.31 and 64.64, H = 4.60 per cent, and on the basis of these analyses pronounced the compound a tetracetate. In the number of acetyl groups present, however, there is a much greater difference in the percentages for four and for five groups, and according to the results of the analyses given above it cannot be doubted that the compound is in reality coerulin pentacetate.

COËRULEIN MONOMETHYL ETHERS.

Coeruleïn (7 grams) and potassium hydroxide (3.5 grams) were dissolved in 150 cc. methyl alcohol and digested for one hour at the boiling-point of the mixture. There was then added an excess of methyl iodide and the whole boiled on a water-bath for twenty hours, adding at intervals of eight hours 2 grams of potassium hydroxide and boiling to make sure of solution, then slight excess of methyl iodide. The excess of methyl iodide and the methyl alcohol were then removed by distillation on a water-bath, the residue treated with 500 cc. of a one per cent solution of potassium hydroxide, and filtered. The insoluble residue will be described below.

The alkaline filtrate was acidified and a heavy dark precipitate was thrown down and filtered out. The precipitate was dissolved in boiling alcohol, filtered, and on standing there were deposited crystals of a dark color, with bronzy luster. The compound decomposes when heated and does not melt. It dissolves in alcohol, acetone, pyridine, aniline, and potassium hydroxide solution, imparting an olive-brown color to the solution in each case.

A determination of methoxy groups gave the following result :

Weight of ether. Gram.	Weight of silver iodide. Gram.	CH_3O. Per cent.
0.2365	0.1703	9.52

Calculated for $C_{20}H_9O_5(OCH_3)$, 8.61 per cent CH_3O.
Calculated for $C_{20}H_8O_4(OCH_3)_2$, 16.58 per cent CH_3O.

The compound is therefore coeruleïn monomethyl ether.

The mother-liquor from which this ether was obtained was allowed to evaporate spontaneously, when another crop of crystals appeared. This compound, when dried and analyzed for methoxy groups, gave the following result:

Weight of substance. Gram.	Weight of silver iodide. Gram.	CH_3O. Per cent.
0.1216	0.0755	8.21

Calculated for $C_{20}H_9O_5(OCH_3)$, 8.61 per cent CH_3O.

It is clearly a coeruleïn monomethyl ether but has different properties from those of the coeruleïn ether described above. It dissolves in acetone and pyridine with a purple color, in alcohol and aniline with a greenish-blue color, in potassium hydroxide solution with a light-green color. It is uniformly more soluble than the isomeric compound already described.

COERULEÏN METHYL ETHER—INSOLUBLE IN ALKALI.

The residue insoluble in alkali (see above under coeruleïn monomethyl ether) was dissolved in alcohol, the solution filtered and concentrated. After standing, a tarry substance was deposited. This was filtered out and the filtrate, which now had a beautiful green fluorescence, allowed to stand for some days. There appeared needle-shaped crystals which were red by transmitted light, green by reflected light. These dissolve with some difficulty in alcohol, giving it a light-purple color; easily in concentrated sulphuric acid with a red color; but they are insoluble in alkalies even on boiling. The quantity of crystals was so small as to make an analysis of the compound impossible, but it is in all probability coeruleïn trimethyl ether.

COERULEÏN MONOETHYL ETHER.

This compound was made in the same way as the monomethyl ether, using ethyl iodide and boiling only nine hours.

It was likewise crystallized from alcohol and had all the characteristics of the corresponding methyl derivative. It was dried at 100° C. and the ethoxy group determined, with the following result :

Weight of ether. Gram.	Weight of silver iodide. Gram.	C_2H_5O. Per cent.
0.1313	0.0808	11.81

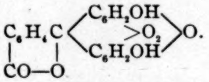
Calculated for $C_{20}H_9O_5(OC_2H_5)$, 12.04 per cent C_2H_5O.

Hence the compound is coeruleïn monoethyl ether.

THEORETICAL.

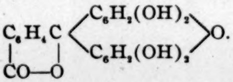
I. GALLEÏN.

The formula for galleïn, as given by Buchka, is



$$\begin{array}{l} C_6H_4C\left\langle\begin{array}{l} C_6H_2OH \\ \qquad >O_2 \\ C_6H_2OH \end{array}\right\rangle O. \\ | \qquad | \\ CO—O \end{array}$$

It is necessary to assume with this formula that oxidation takes place in the process of making galleïn, giving rise to a quinone group. This idea was first suggested to him by the supposed discovery of the so-called hydrogalleïn, which he regarded as a reduction-product intermediate between galleïn and gallin. Hydrogalleïn, according to Buchka, differs essentially from both galleïn and gallin, but gives the same product when acetylized as that obtained from galleïn by acetylization. In order to account for this, he gave galleïn the above formula and to hydrogalleïn the formula :



$$\begin{array}{l} C_6H_4C\left\langle\begin{array}{l} C_6H_2(OH)_2 \\ C_6H_2(OH)_2 \end{array}\right\rangle O. \\ | \qquad | \\ CO—O \end{array}$$

The necessity for providing a formula for hydrogalleïn was the single consideration that led him to assign to galleïn the above formula.

Many attempts were made during the progress of this work to prepare hydrogalleïn and its acetate. The result was always the same—the hydrogalleïn acetate invariably proved to be identical in every respect with gallin acetate. Attempts were made also to make gallol acetate by Buchka's method—reduction of galleïn in acid solution by zinc dust, and acetylization of the product thus obtained. Here again the so-called gallol acetate was identical with gallin acetate. The identity of these three acetates is clearly shown not only by analyses but also by identity of melting-point and by their conduct with sodium carbonate solution, with concentrated sulphuric acid, and with silver nitrate solution. So that no matter whether galleïn be reduced by zinc dust in acid or alkaline solutions, hot or cold, the product is in all cases gallin, which, with acetic anhydride, yields gallin tetracetate. The existence of hydrogalleïn is, therefore, extremely improbable, and it is doubtful if gallol or its acetate has been isolated. The conclusion here stated with reference to hydrogalleïn is in entire accord with Herzig's work, to which reference has already been made.

That galleïn contains a carboxyl group is proved by the fact that it forms esters in the ordinary way. Methyl and ethyl esters have both been prepared. Further, galleïn forms a stable ammonium salt,[1] which suffers no loss of ammonia after prolonged heating, in this respect showing a marked difference from phenolphthaleïn. Galleïn also decomposes sodium, barium, and calcium carbonates, driving out carbon dioxide and forming soluble compounds with the metals. The presence of the carboxyl group may explain, also, why galleïn is converted more easily than other phthaleïns into its corresponding phthalideïn, since there is no lactone ring in this compound. This will be referred to again in the theoretical discussion of coeruleïn.

The formation of the colored tetramethyl and tetraethyl ethers, which are easily saponified to the colorless triethers with alkalies, also proves the presence of a carboxyl group in galleïn. The existence of the blue basic lead salt and of the colored galleïn triphenyl carbamate, which has acid properties, indicates the same thing.

That galleïn contains only three phenolhydroxyl groups is shown by the introduction into its molecule of three phenylisocyanate groups. It has been established, notably by Goldschmidt,[1] that phenyl isocyanate does not react with quinone oxygen, but easily with hydroxyl hydrogen, except when present in carboxyl groups. The galleïn triphenylcarbamate has a color and dissolves in a cold solution of sodium carbonate with color. Hence it must contain a carboxyl group, but cannot be a derivative of gallin (formed by reduction). Since, therefore, galleïn, in free condition, contains one carboxyl and three phenolhydroxyl groups, its structure must be:

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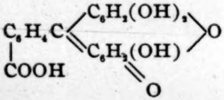
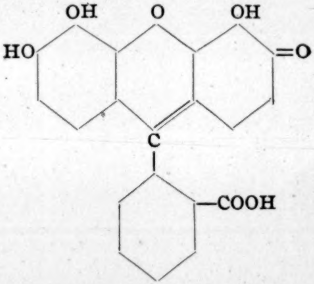
[1] Buchka: Ann. Chem. (Liebig), 209, 263.

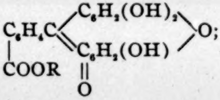


$$\underset{\mathrm{COOH}}{\underset{|}{\mathrm{C_6H_4}}}\mathrm{C}\begin{matrix}\diagup\mathrm{C_6H_2(OH)_2}\diagdown\\ \diagdown\!\!\diagdown\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C_6H_2(OH)}}\diagup\end{matrix}\mathrm{O}$$

or

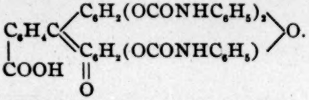


The quinoid structure would explain the deep-red color of galleïn and its solutions. According to this formula the structure of the highly colored methyl or ethyl ester would be



$$\underset{\mathrm{COOR}}{\underset{|}{\mathrm{C_6H_4}}}\mathrm{C}\begin{matrix}\diagup\mathrm{C_6H_2(OH)_2}\diagdown\\ \diagdown\!\!\diagdown\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C_6H_2(OH)}}\diagup\end{matrix}\mathrm{O};$$

and for the colored triphenyl carbamate having acid properties,



$$\underset{\mathrm{COOH}}{\underset{|}{\mathrm{C_6H_4}}}\mathrm{C}\begin{matrix}\diagup\mathrm{C_6H_2(OCONHC_6H_5)_2}\diagdown\\ \diagdown\!\!\diagdown\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C_6H_2(OCONHC_6H_5)}}\diagup\end{matrix}\mathrm{O}.$$

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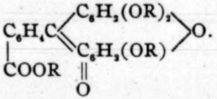
[1] Ber. d. chem. Ges., 22, 3105.

This formula for galleïn explains also the formation and properties of its colored tetramethyl and tetraethyl ethers. These would be represented thus :



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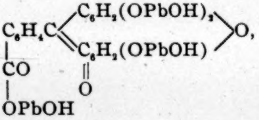
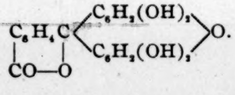
A compound with such a structure one would expect to be colored and to lose one alkyl group by saponification. As a matter of fact these ethers are colored (deep-red), and are saponified by sodium carbonate or hydroxide leaving a trialkyl ether. The deep-blue basic lead salt probably has the following formula :

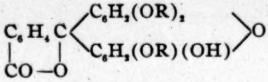


and the blue potassium salt, which is precipitated when a saturated alcoholic solution of galleïn and a saturated alcoholic solution of caustic potash are mixed, probably has a similar structure, the metal potassium replacing the PbOH groups.

There are compounds, however, which seem to be derived from a tautomeric form of galleïn. This would have the lactoid structure and be represented thus :

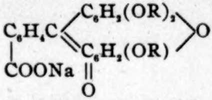


To this class belong the trimethyl and triethyl ethers which, when uncombined, are colorless, but dissolve in sodium carbonate with a red color. The relation between the free ethers and their alkali salts appears to be the same as that between phenolphthaleïn and its salts. This relation is shown in the following formulas :



$$\begin{array}{l} C_6H_4C\left<\begin{array}{l}C_6H_2(OR)_2\\ C_6H_2(OR)(OH)\end{array}\right>O \\ |\qquad\;\; | \\ CO-O\end{array}$$

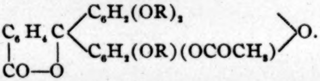
I. Galleïn trialkyl ether. (Colorless.)



$$\begin{array}{l} C_6H_4C\left<\begin{array}{l}C_6H_2(OR)_2\\ C_6H_2(OR)\end{array}\right>O \\ | \\ COONa \;\; \| \\ \qquad\quad\;\; O\end{array}$$

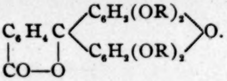
II. Sodium salt of galleïn trialkyl ether. (Red.)

That Formula I. above, correctly represents the structure of the galleïn trialkyl ethers is indicated further by the fact that they can be readily acetylized as well as transformed into the colorless tetralkyl ethers. The products thus obtained are also colorless. Since the hydrogen atom is replaced by this process, the trialkyl gallein acetate is insoluble in alkalies except on prolonged boiling, which results in saponification of the acetyl group. These characteristics accord with the following structure for the trialkyl gallein acetate,



$$\begin{array}{l} C_6H_4C\left<\begin{array}{l}C_6H_2(OR)_2\\ C_6H_2(OR)(OCOCH_3)\end{array}\right>O. \\ |\qquad\;\; | \\ CO-O\end{array}$$

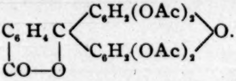
The conception of galleïn as a tautomeric substance finds support also in the existence of two classes of tetralkyl ethers —one, the quinoid (colored), already referred to; the other, the lactoid (colorless), which would have this structure:



$$\begin{array}{l} C_6H_4C\left<\begin{array}{l}C_6H_2(OR)_2\\ C_6H_2(OR)_2\end{array}\right>O. \\ |\qquad\;\; | \\ CO-O\end{array}$$

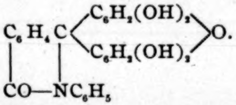
With such a structure one would expect them to be colorless and unaffected by alkalies. Both of these characteristics they were found to possess.

The acetate and the benzoate of galleïn would properly be derived from its lactoid modification, since they are colorless and (at least in the acetate) are known to contain four acid residues. Letting Ac represent the acid residue, they would have the structure



$$\begin{array}{l} C_6H_4C\left<\begin{array}{l}C_6H_2(OAc)_2\\ C_6H_2(OAc)_2\end{array}\right>O. \\ |\qquad\;\; | \\ CO-O\end{array}$$

Galleïn anilide, a colorless compound, made by Albert,[1] should be a derivative of the lactoid modification also and have the structure :[2]



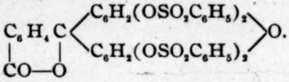
$$\begin{array}{l} C_6H_4C\left\langle \begin{array}{l} C_6H_2(OH)_2 \\ C_6H_2(OH)_2 \end{array} \right\rangle O. \\ \;| \qquad | \\ CO—NC_6H_5 \end{array}$$

The colorless methyl ether which he made from the anilide and called a dimethyl ether is very probably a tetramethyl ether. By combustion-analysis he found carbon = 72.72 per cent, hydrogen = 4.58 per cent.

	Calculated for	Per cent C.	Per cent H.
Di-ether	$C_{28}H_{19}O_6N$[3]	72.25	4.08
Tetra-ether	$C_{30}H_{25}O_6N$	72.70	5.08

From the above it is seen that this compound is more probably a tetraether than a diether.

Another of the lactoid derivatives of galleïn is the tetrabenzenesulphonate described by Georgescu.[4] He gives it the diketone formula which has been abandoned for all phthaleïns. It more probably has the structure



$$\begin{array}{l} C_6H_4C\left\langle \begin{array}{l} C_6H_2(OSO_2C_6H_5)_2 \\ C_6H_2(OSO_2C_6H_5)_2 \end{array} \right\rangle O. \\ \;| \qquad | \\ CO—O \end{array}$$

Galleïn, then, is tautomeric, yielding two classes of derivatives, those with color having the quinoid structure, and colorless derivatives with the lactoid structure. Free galleïn has the quinoid structure.

The formation of the anhydride of pyrogallol ketone and benzoic acid, by fusing galleïn with caustic potash, as described by Buchka, finds a very easy explanation if we adopt the above formula for galleïn. This is shown in the following equation :

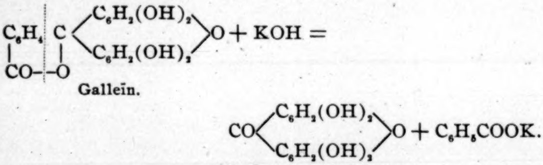
---

[1] Ber. d. chem. Ges., 27, 2794. The fact that this compound and its methyl ether are colorless makes it certain that they do not contain quinone groups and hence do not have the formulas given them by Albert.

[2] The position of the $>NC_6H_5$ group in this compound has not yet been determined.

[3] This is the formula for the dimethyl ether of galleïn anilide according to Buchka's formula.

[4] Bulletinul Societatii De Sciinte Fizice d. Bucuresci Romănia, 1, 215.

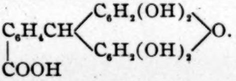


$$\underset{CO-O}{C_6H_4\cdot C}\Big\langle{}^{C_6H_2(OH)_2}_{C_6H_2(OH)_2}\Big\rangle O + KOH = CO\Big\langle{}^{C_6H_2(OH)_2}_{C_6H_2(OH)_2}\Big\rangle O + C_6H_5COOK.$$

Galleïn.

Anhydropyrogallol ketone.

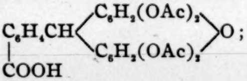
The structure of gallin is established in a measure by its relation to galleïn, from which it is derived by the addition of two atoms of hydrogen. This probably reduces the quinoid group with simultaneous loss of color, and the product is doubtless properly represented thus :



$$\underset{COOH}{C_6H_4CH}\Big\langle{}^{C_6H_2(OH)_2}_{C_6H_2(OH)_2}\Big\rangle O.$$

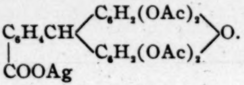
Gallin.

In support of this view of its structure is its easy transformation into the colorless tetracetate, a compound with acid properties. This characteristic the acetate shows not only in dissolving readily in sodium carbonate solution, but also in forming a silver salt. The structure of gallin acetate and its silver salt is shown in the following formulas :



$$\underset{COOH}{C_6H_4CH}\Big\langle{}^{C_6H_2(OAc)_2}_{C_6H_2(OAc)_2}\Big\rangle O;$$

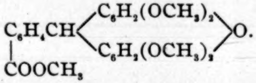
Gallin acetate.



$$\underset{COOAg}{C_6H_4CH}\Big\langle{}^{C_6H_2(OAc)_2}_{C_6H_2(OAc)_2}\Big\rangle O.$$

Silver salt of gallin acetate.

A further proof of the correctness of this view of the structure of gallin is the formation of a pentamethyl derivative by the action of methyl iodide upon an alkaline solution of gallin. It probably has the following structure:

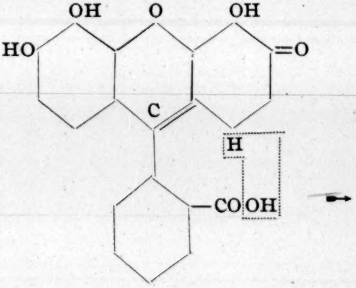


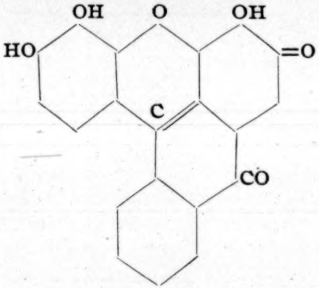
$$\begin{array}{l} C_6H_4CH\left\langle\begin{array}{l}C_6H_2(OCH_3)_2\\ C_6H_2(OCH_3)_2\end{array}\right\rangle O.\\ \mid\\ COOCH_3\end{array}$$

As was to be expected, this ether, though insoluble in cold alkalies, may be saponified by heating in alkali solutions, forming a product easily soluble in sodium carbonate solution without color.

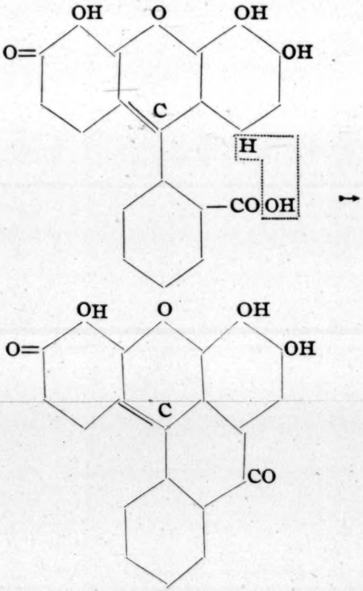
II. COERULEÏN.

Coeruleïn is the phthalideïn of galleïn and sustains to it the same relation that phenolphthalideïn bears to phenolphthaleïn. Baeyer, in his work on phenolphthalideïn, found that when it was distilled with zinc dust, it yields phenylanthracene. Buchka obtained the same product by distilling coeruleïn with zinc dust. Since coeruleïn is derived from galleïn, probably by the loss of one molecule of water, and since, according to Buchka's work, it is a derivative of phenylanthracene, it would seem that the hydroxyl group of the phthalic acid residue in galleïn unites with one of the hydrogen atoms of one of the pyrogallol residues to form water, the readjustment of affinities taking place as represented in the following formulas:

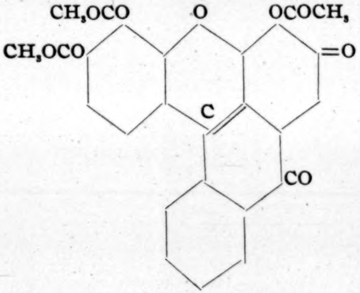




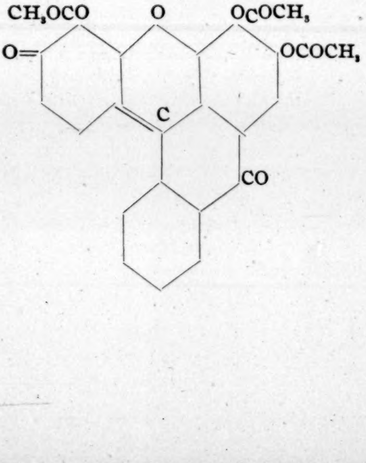
or



That the carboxyl group of galleïn takes part in the reaction is indicated by the fact that, while galleïn is easily soluble in sodium carbonate solution, coeruleïn is insoluble in such a solution. The presence of a carboxyl group in galleïn explains the easy formation of coeruleïn, compared with other phthalideïns. This formula for coeruleïn is also in accord with the fact that when all the oxygen atoms in coerulein are replaced by hydrogen, by means of zinc dust, phenylanthracene is formed. It easily explains how coeruleïn forms a triacetate easily reduced with zinc dust in acetic acid solution. Such a derivative would be represented thus :

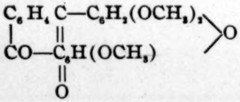


or

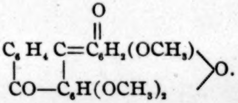


With the formulas given above for coeruleïn there is a possibility of having three varieties of monalkyl ethers. Two monomethyl ethers are described in the experimental part of this paper. It is impossible at present to determine the exact position of the methyl group in these ethers. They are readily soluble in alkalies—a characteristic they could not show if only one hydroxyl group were present in coeruleïn, as represented in Buchka's formula for this compound. Again the fact that there are two monoethers requires that more than one hydroxyl group be present in the molecule.

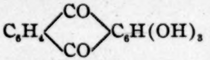
A methyl ether was made, which was entirely insoluble in alkalies, even on boiling, but in such small amounts as to make analysis impossible. This was probably coeruleïn trimethyl ether. It would have the structure



or

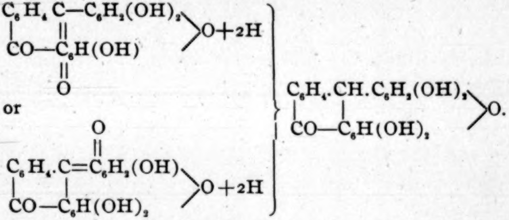


Coeruleïn thus appears as a derivative of anthragallol,

 1.2.3,

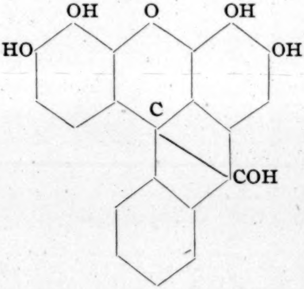
which, like coeruleïn, is soluble in alkalies with a green color. This will explain why coeruleïn resembles alizarin and anthragallol in its property of forming insoluble lakes with chromium, iron, and aluminium mordants. The name, alizarin-green, by which coeruleïn is known, recalls this fact, which has long been known to the dyer. The above formula for coeruleïn also serves to recall the aurin group of dyestuffs, to which it shows certain resemblances.

Coerulin is derived from coeruleïn by addition of two hydrogen atoms. This would probably result first in reducing the quinoid group, thus :

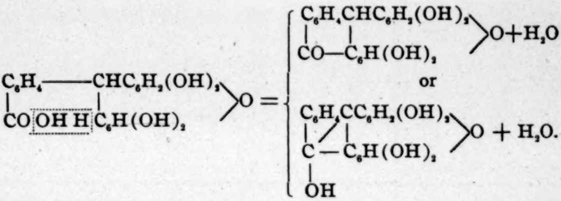


$$\left.\begin{array}{l}\left.\begin{array}{l}C_6H_4\,C{-}C_6H_2(OH)_2\\ |\qquad\;\|\\ CO{-}C_6H(OH)\\ \qquad\;\|\\ \qquad\;O\end{array}\right\rangle O+2H\\ \text{or}\\ \left.\begin{array}{l}\qquad\quad O\\ \qquad\quad\|\\ C_6H_4.C{=}C_6H_2(OH)\\ |\qquad\;|\\ CO{-}C_6H(OH)_2\end{array}\right\rangle O+2H\end{array}\right\}\left.\begin{array}{l}C_6H_4.CH.C_6H_2(OH)_2\\ |\qquad\;|\\ CO{-}C_6H(OH)_2\end{array}\right\rangle O.$$

The reduced product would be expected to go over to its more stable form and become:



Coerulin is formed also from gallin by the action of concentrated sulphuric acid in the cold. This transformation may be represented thus:



$$\left.\begin{array}{l}C_6H_4{-\!-\!-}CHC_6H_2(OH)_2\\ |\qquad\qquad|\\ CO\boxed{OH\;H}C_6H(OH)_2\end{array}\right\rangle O=\left\{\begin{array}{l}\left.\begin{array}{l}C_6H_4CHC_6H_2(OH)_2\\ |\qquad\;|\\ CO{-}C_6H(OH)_2\end{array}\right\rangle O+H_2O\\ \qquad\qquad\text{or}\\ \left.\begin{array}{l}C_6H_4CC_6H_2(OH)_2\\ |\;/\;|\\ C{-}C_6H(OH)_2\\ |\\ OH\end{array}\right\rangle O+H_2O.\end{array}\right.$$

In favor of this view of the structure of coerulin is the fact that it forms a pentacetate with acetic anhydride.

The more important facts brought out in this paper may be found in the following summary:

SUMMARY.

1. The only reduction-product of galleïn by zinc dust, whether in acid or alkaline solution, is gallin.

2. Galleïn forms monoesters, showing that it contains one carboxyl group.

3. Three phenyl isocyanate groups may be introduced into a molecule of galleïn, proving that it contains three phenol hydroxyl groups.

4. Two classes of tetralkyl ethers, colored and colorless, are derivable from galleïn, indicating that it reacts in tautomeric modifications.

5. Galleïn yields a colorless tetracetate, as shown by making determinations of the number of acetyl groups introduced. This proves that galleïn may act as a tetracid phenol.

6. Colorless trialkyl derivatives of galleïn, which resemble phenolphthaleïn, are described.

7. A colorless trimethyl galleïn monacetate is described.

8. Gallin pentamethyl ether and gallin tetracetate furnish evidence as to the structure of gallin.

9. A silver salt of gallin tetracetate also furnishes evidence as to the structure of gallin.

10. Coeruleïn is shown to form a triacetate—by making determinations of the number of acetyl groups introduced.

11. Coeruleïn forms two monomethyl ethers, and a methyl ether insoluble in alkalies; likewise a monoethyl ether.

12. Coerulin forms a pentacetate, as shown by making determinations of the number of acetyl groups introduced.

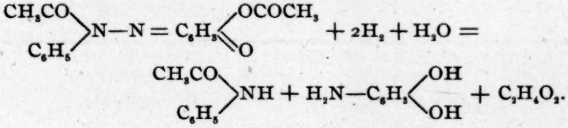
CORNELL UNIVERSITY,
ITHACA, N. Y.,
March, 1901.

ON THE TWO MODIFICATIONS OF BENZENE-4-AZORESORCIN AND THE CONSTITUTION OF THE OXYAZO COMPOUNDS.

BY W. R. ORNDORFF AND E. D. THEBAUD.

In 1887 Will and Pukall[1] found that benzene-4-azoresorcin, $C_6H_5N_2C_6H_3(OH)_2(1,2,4)$, could be obtained in two modifications, one melting at 161° and crystallizing from dilute alcohol in long, reddish-yellow needles, the other melting at 170° and crystallizing from ordinary alcohol in short, dark-red needles. They also found that each modification could be converted into the other at will by using either strong or dilute alcohol as the solvent.

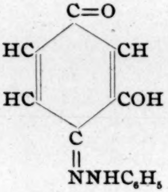
In 1892 Goldschmidt and Pollak[2] showed that the diacetyl derivative of the modification melting at 161° gave, on reduction with zinc dust and acetic acid, acetanilide and amidoresorcin in accordance with the following equation:



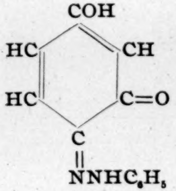
$$\left.\begin{matrix}CH_3CO\\C_6H_5\end{matrix}\right\rangle N-N=C_6H_3\left\langle\begin{matrix}OCOCH_3\\O\end{matrix}\right. + 2H_2 + H_2O =$$

$$\left.\begin{matrix}CH_3CO\\C_6H_5\end{matrix}\right\rangle NH + H_2N-C_6H_3\left\langle\begin{matrix}OH\\OH\end{matrix}\right. + C_2H_4O_2.$$

They, therefore, conclude that benzene-4-azoresorcin is a hydrazone quinone and not an oxyazo compound, and that it must have one of the two following formulas, according as it is considered a para- or an orthoquinone derivative:



I.



II.

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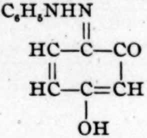
[1] Ber. d. chem. Ges., 20, 1119.

[2] *Ibid.*, 25, 1342.

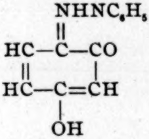
They give the preference to the second formula on account of the easy transformation of the diacetyl derivative into acetanilide and amidoresorcin on reduction, and because the acetyl derivatives of paraoxyazo bodies are only reduced to hydrazo compounds by such treatment.

If this view of Goldschmidt and Pollak be correct, then two stereoisomeric phenylhydrazones of formula II should be possible, as follows :



I.

and



II.

As there are two modifications of benzene-4-azoresorcin, which may be converted one into the other with the greatest ease, it seemed quite likely that we have here to deal with a case of stereoisomerism, such as has been observed already in the case of a number of unsymmetrical phenylhydrazone derivatives. The following investigation was undertaken to test this hypothesis and incidentally to add something to our knowledge of the constitution of the oxyazo compounds.

Benzene-4-azoresorcin was made and purified according to the method of Will and Pukall.[1] It was then recrystallized from 35 per cent alcohol and from ordinary alcohol, and both modifications described by these authors were obtained. The statements made by them in regard to these products were confirmed in every particular. On analysis by the Dafert modification of the Kjeldahl method the products gave the following results :[2]

Weight of substance. Gram.	Weight of NH_3 found. Gram.	Per cent N found.	Calculated for $C_{12}H_{10}N_2O_2$.
0.0924	0.0147655	13.14	13.11
0.0910	0.0145418	13.14	....

[1] Ber. d. chem. Ges., **20**, 1121.

[2] The atomic weights used in this paper are those recommended by the German Chemical Society. See Ber. d. chem. Ges., **31**, 2761 (1878).

It has been shown by Hewitt, Moore, and Pitt[1] that many azo compounds contain water of crystallization, which they give up on standing over sulphuric acid in a vacuum-desiccator or on heating in an air-bath to 70°. As the modification of benzene-4-azoresorcin, melting at 161°, is obtained by crystallizing the modification melting at 170° from dilute alcohol, it was thought possible that it might contain water of crystallization, and for this reason melted at a lower temperature. But it was found to lose no weight when kept in a Hempel vacuum-desiccator for forty-eight hours or when heated in an air-bath to 110° to 120° for several hours. Hence the modification melting at 161° does not contain water of crystallization. The modification melting at 170° was then treated in the same way and was also found to lose no weight. It, hence, contains neither alcohol nor water of crystallization.

When recrystallized from benzene both modifications yield only the product melting at 170°.

It was not found possible to determine the molecular weight of the two modifications, owing to the ease with which one form changes into the other, but it is extremely probable, from the method of formation and the remarkable ease with which they are converted into each other, that they are metameric substances and are both correctly represented by the formula $C_{12}H_{10}N_2O_2$. Both modifications give the same diacetyl product, melting at 104°, when heated with acetic anhydride and fused sodium acetate. From these facts it seems highly probable that the two modifications have the same structure and are therefore stereo- or space-isomers, corresponding to the formulas given above. A similar case of stereoisomerism is seen in the two modifications of the phenylhydrazone derivative of salicylic aldehyde, $HOC_6H_4CH = N.NHC_6H_5$, melting at 142° and 104°–105°. The lower melting form is converted into the higher one by warming with alcohol.

We next endeavored to determine whether this stereoisomerism could be shown to exist in the derivatives of benzene-4-azoresorcin. For this purpose the diacetyl product melting at 104° was carefully recrystallized from 35 per cent alcohol.

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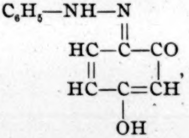
[1] Ber. d. chem. Ges., 31, 2114.

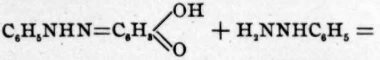
The product obtained melted at 106° and had a reddish-yellow color, whereas the product recrystallized from ordinary alcohol melted at 104° and had a pure yellow color.

The monoethyl ether of benzene-4-azoresorcin was then made and purified according to the method of Will and Pukall.[1] From ordinary alcohol it crystallized in short, brownish-red needles which melted at 87°. When this product was recrystallized from dilute alcohol (35 per cent), it gave long, reddish-yellow needle-shaped crystals, which melted at 88°. Although the difference in melting-point was only 1°, the difference in color was much more marked than in the case of the two modifications of benzene-4-azoresorcin.

If benzene-4-azoresorcin is in reality a phenylhydrazone derivative of an oxyquinone, as held by Goldschmidt and Pollak and as shown in the following formula,



it should react with phenylhydrazine to give a bisphenylhydrazone, thus:



$$C_6H_5NHN{=}C_6H_3\begin{matrix}\diagup OH \\ \diagdown O\end{matrix} + H_2NNHC_6H_5 =$$

$$(C_6H_5NHN{=})_2C_6H_3OH + H_2O.$$

In order to make this substance we first made a diacetyl product from benzene-4-azoresorcin and dissolved this in glacial acetic acid. An excess of phenylhydrazine was then added and the mixture heated to boiling for a few minutes. On the addition of water a precipitate formed. This was filtered off, washed thoroughly, dried, and recrystallized from benzene. The product thus obtained had a deep-red color, crystallized in rounded grains and melted sharply at 163°. The substance was analyzed by the Dafert modification of the Kjeldahl method and gave the following results:

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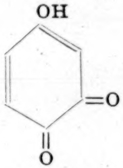
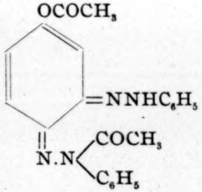
[1] Ber. d. chem. Ges., 20, 1146.

Weight substance. Gram.	Weight of NH_3 found. Gram.	Per cent N found.	Calculated for $C_{22}H_{20}N_4O_3$.
0.0377	0.006615	14.43	14.46
0.0447	0.00784325	14.43	....

The substance is therefore the diacetyl derivative of the bis-phenylhydrazone of the oxyquinone:



and has the following structural formula:

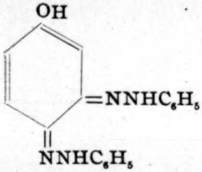


The diacetyl product was then saponified with alcoholic caustic potash, the product precipitated with water, the precipitate washed thoroughly with water and recrystallized from hot dilute acetic acid. The product thus obtained crystallizes in dark-red needles, which melt sharply at 160°. An analysis by the Dafert-Kjeldahl method gave the following result:

0.3941 gram substance gave 0.07132976 gram nitrogen.

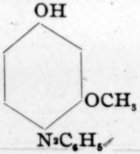
	Calculated for $(C_6H_5{-}NH.N{=})_2(C_6H_3OH)$.	Found.
N	18.45	18.10

The product is, hence, the bis-phenylhydrazone of the oxyquinone and must have the following formula:



It is soluble in caustic potash solution and in hydrochloric acid, in benzene, ether, chloroform, and alcohol, but acetic acid is the best solvent from which to recrystallize it. In concentrated sulphuric acid it dissolves with a reddish-brown color, and on reduction with zinc dust in acetic-acid solution it gives aniline and a product which gives a red color with a solution of bleaching-powder and also with ferric chloride solution. The addition of an excess of caustic potash solution to the acetic acid solution of the reduction-products gave a deep-blue color, which became green on standing, or more quickly on shaking with air. Owing to the extreme instability of this reduction-product it was impossible to isolate it and determine whether it was a diamidophenol or not. Aniline was isolated, however, and identified by its characteristic reactions, and it is probable that the other product was 1,3,4-diamidophenol, as it gave the characteristic color reactions of this substance.

We then tried to prepare the orthomonomethyl ether of benzene-4-azoresorcin.



A monomethyl ether of benzene-4-azoresorcin has already been prepared by Will[1] by the action of caustic potash and methyl iodide on benzene-4-azoresorcin. This author found it extremely easy to make the monoethers, but very difficult to prepare the diethers. From the method of preparation of this monomethyl ether of Will it seems quite probable that it has the following formula:

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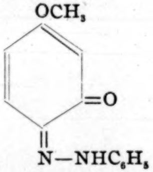
[1] Ber. d. chem. Ges., **21**, 604.



This formula would explain very simply the great difficulty Will found in preparing the diethers of benzene-4-azoresorcin.

We prepared this ether by the method of Will. It was a red crystalline product which, when carefully purified by recrystallization from ordinary alcohol, melted at 123° and not at 114°, as given by Will.

The method by which we attempted to prepare the ortho ether was as follows: The monomethyl ether of resorcin, boiling at 243° to 244°, was first prepared and purified according to the method of Tieman and Parrisius.[1] This ether was dissolved in alcohol and treated with the theoretical amount of diazobenzene chloride in dilute alcohol, to convert it into the azo compound. After standing for half an hour the mixture was poured into an alcoholic solution of sodium acetate. A red crystalline product separated out. This was filtered off, washed with water, and recrystallized twice from alcohol. Finally it was recrystallized from a mixture of chloroform and alcohol. The product crystallized in short, red needles, melting at 189° to 190°. Analyses by the Dafert-Kjeldahl method gave the following results:

I. 0.0585 gram substance gave 0.01205476 gram NH_3.

II. 0.0576 gram substance gave 0.01158253 gram NH_3.

	Calculated for $(C_6H_5N_2)_2C_6H_2{<}^{OH}_{OCH_3}$.	Found.	
		I.	II.
N	16.90	16.95	16.54

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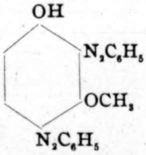
[1] Ber. d. chem. Ges., 13, 2363.

The product is, hence, the monomethyl ether of resorcindisazobenzene. As it is formed under similar conditions to those which gave Kostanecki his resorcin disazobenzene, (2,4), and is soluble in caustic potash solution, it probably has a similar structure:



Contributions from the Sheffield Laboratory of Yale University.

LXXVIII.—ON THE PERIODIC SYSTEM AND THE PROPERTIES OF INORGANIC COMPOUNDS.

II.—Gradations in the Properties of Alums.

By James Locke.

In my first paper on this subject[1] I attempted to show that the well-known difficulties which confront the chemist in classifying the elements and their compounds according to the Periodic System are confined practically to the latter class of substances. That there is a definite connection between the properties of an element and those of its compounds is, of course, obvious from the numerous cases in which both fulfil the requirements of the system, But, to take one of the chief difficulties, there are almost no instances in which, when an element can appear in more than one degree of oxidation, the properties of its compounds in each type find accurate interpretation by the System. As a case in point may be cited nitric acid, the nitrates, and nitrous acid and the nitrites, as compared respectively with the derivatives of the pentoxide and trioxide of phosphorus. So far as their oxygen compounds are concerned, the two elements have in neither the quinquivalent nor trivalent state anything in common, except their valence and acid-forming nature. In crystallographic form, solubility, even in formulas, their derivatives are inherently different. Nitrogen pentoxide is a volatile liquid; phosphorus pentoxide a non-volatile solid. The former forms only the monobasic acid, HNO_3; the latter yields preferably polybasic acids. The normal nitrates are in every case readily soluble in water. The normal phosphates, pyrophosphates, and metaphosphates are in almost every case insoluble in water.

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[1] This Journal, 20, 581.

With the trioxides the degree of similarity is about the same—strict analogy is practically absent. But, nevertheless, such a loose periodic system worship prevails, that almost every modern text-book on inorganic chemistry contains a stereotyped statement that nitric acid is analogous to phosphoric acid. In some instances even these bounds have been far overstepped. Probably the most thoroughly systematized smaller work on the subject is that of Professor Ramsay. On pages 333ff of his "System of Inorganic Chemistry" (1891) he classes nitrogen tetroxide with vanadium tetroxide, nitrous acid with vanadious hydroxide. The latter two are apparently analogous because they have the analogous formulas, $NO(OH)$ and $VO(OH)$. If this is enough for chemical analogy, why should not the aluminium compound $AlO(OH)$ be put in the same class? Aluminium and vanadium both form alums, and, as he emphasizes of vanadium hydroxide, both unite with the alkalies. I speak of this, not in criticism of Professor Ramsay's book, but in protest against the all-prevailing tendency to go a-begging for chemical analogy when the system requires it.

The term "chemical character of an element" has two very different meanings. In the first place it denotes the behavior of the element itself, in the free state; in the second, the type of reactions of its compounds. In the latter case we may perhaps use an explanatory prefix, and say, for instance, "the character of *ferric* iron" or of *ferrous* iron. The two terms denote two absolutely different states of matter. When one speaks of ferric iron, the mind involuntarily associates it, not with ferrous iron nor metallic iron, but with the salts of aluminium and trivalent chromium; with two elements which in the free state bear no analogy to metallic iron,[1] and no relation between which and iron is shown by the System. The simplest and most natural analogues of ferric iron are merely the trivalent ions of aluminium and chromium. On the other hand, "ferrous iron" brings to the mind, in addition to the idea of something readily oxidizable, the thought of magnesium and zinc compounds—derivatives of elements which again have nothing in common with metallic iron, and also no resemblance to the metals with which iron in the trivalent state is analogous. Unless a very strong distinction is made between the different usages of the term "chemical character of iron," therefore, this brings about a state of hopeless confusion. Up to the present time it certainly has led to a marked subordination, in importance, of compounds containing elements in unstable states of valence to those in which they are stable. Practically, this is all very well. But from the theoretical standpoint it places a direct obstacle in the way of careful and systematic interpretation of fact, for it makes, in such cases, the power of oxidation or reduction much more important than the simple properties of the compounds as such.

The laws of electricity cease to obtain, as soon as that force has been converted into light, or heat, or chemical energy—no matter which. But ferric iron and ferrous iron are just as distinct primary forms of matter as these are distinct forms of energy. Like the latter, they may be converted, the one into the other, or they may be converted into metallic iron. But whether a ferric salt passes into a ferrous salt, or into metallic iron, the form of matter analogous to aluminium in the combined state ceases to exist. What it becomes, and how readily it undergoes alteration, are questions common to all the ferric compounds, and should be theoretically regarded as belonging to a set of problems entirely distinct and separate from those involving the individual salts.

In order clearly to characterize an element in a given degree of oxidation, the first step should be, not to ascertain how stable or unstable its compounds are, but how nearly they approach, in their physical properties, solubility, etc., the corresponding salts of other elements of the same valence. Such arbitrary conditions as, for instance, the presence of oxygen in working with easily oxidizable substances, should be avoided. And, furthermore, the questions of analogy should be decided along strict lines. The rare-earth metals are, more often than not, spoken of as analogous to aluminium. But the two notable properties which characterize the aluminium salts—the extremely weak basicityof the hydroxide, with the corresponding readiness to form basic salts, and the marked tendency to form complex ions (still more highly developed in chromium and ferric iron), as illustrated in the behavior of aluminium solutions containing oxalic, tartaric, or other organic acids,—are just the reverse of the properties which characterize the strongly basic rare earths. In Dammer's Handbuch we find specific mention of fourteen derivatives of aluminium chloride. Under cerous chloride—the chlorine compound of the best investigated rare earth, we find but two.[1] Barium chloride and cupric chloride show a similar difference. In both cases the divergence is due to very much the same cause. The very nature of the strongly basic ions of barium and cerium prevent the formation of such derivatives; and since the divergence in the behavior of the chlorides is duplicated in that of sulphates, nitrates, bromides, and countless other salts, it surely indicates a radical distinction in the character of cerium and aluminium, to which much more weight should be attached than to the fact that the hydroxides of both are flocculent precipitates. The latter resemblance is essentially the basis of assertions that they are analogous. Cerium may be regarded as the prototype of the rare-earth metals; aluminium as that of trivalent chromium, manganese, vanadium, iron, cobalt, and others. In each group the reactions of these typical metals are closely followed by all their respective members in a way which proves that the separate reactions of each are not to be regarded as individual functions of the elements, but closely correlated with one another. For instance, it means that a trivalent metal which forms alums will yield complex tartrate ions, and that a trivalent metal whice has a strongly basic hydroxide will form an insoluble oxalate, and not form an alum nor a double chloride with potassium chloride, but that its oxide will dissolve readily in dilute acids.

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[1] By this I mean the strong analogy which is exhibited between free elements belonging to the same family and sub-group in the System; for example, metallic zinc nd cadmium, silver and gold, arsenic and antimony, etc.

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[1] Exclusive of the platinichloride, etc.

As illustrations in the above, I have chosen the trivalent metals by chance. Others would have done just as well. If we compare the solubility relations and, exclusive of those in which a change of valence takes place, the reactions, of cuprous compounds, with those of the corresponding silver salts, we find an almost exact similarity between the two. But to ascertain experimentally in how far the strict classification of the elements in the manner indicated is possible, the trivalent metals are especially suitable. Among the alum-forming elements we find one (cobalt) which in the trivalent state yields compounds that are very unstable because of the high valence; and a second one (vanadium) whose compounds are equally unstable because of the abnormally low valence. The range of the atomic weights of the alum-forming trivalent metals, from 27 (Al) to 114 (In), is also exceptionally great for an isomorphous series, and these elements constitute members of six out of the eight families in the system.

The total number of trivalent elements entering into the compounds $M^IM^{III}(SO_4)_2.12H_2O$ is eight: aluminium, titanium, vanadium, chromium, manganese, iron, cobalt, gallium, and indium. Of univalent elements, M^I represents five: sodium, potassium, rubidium, caesium, thallium; and also the ammonium, hydroxylammonium, methylammonium, etc., radicals.[1]

A cursory glance over the literature shows at once that there is a more or less pronounced decrease in stability with increasing atomic weight of the trivalent metal in an alum, and apparently that the heavier the univalent metal the greater will be the stability. Thus, sodium enters into alums only with the lightest of the trivalent metals—aluminium, vanadium, and chromium. The only stable potassium alums are those of aluminium and chromium; potassium-ferric and potassium-gallium alums break down into basic salts very readily, and the only double sulphates of potassium and indium which can be obtained have the formulas

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[1] The existence of the silver aluminium alum described by Church and Northcote is denied by Retgers.

$$KIn(SO_4)_2.4H_2O \quad \text{and} \quad K_2SO_4.2In_2(SO_4)_3.6H_2O.$$

The only alums which have as yet been obtained of titanium are those in which the univalent metal is caesium or rubidium.[1] After much doubt had been cast upon the existence of the manganese alums described by Mitscherlich, Piccini has shown that at least the caesium compound of this element can be easily obtained.[2] Owing to the great instability of their salts, and the correspondingly slight value which could be attached to measurements of their physical constants, I have felt it useless to include these metals in the present investigation, which covers, however, alums of all the other trivalent metals mentioned above, except gallium.

I have also rejected the salts of the substituted amines, as involving the ulterior question of the influence of complex radicals. The ammonium alums, however, in view of their frequent occurrence, have been carefully studied, in order to ascertain how far the generally greater readiness of this complex to yield double salts, as compared with that of potassium, is capable of exact determination. The univalent groups studied, therefore, were sodium, potassium, ammonium, rubidium, caesium, and thallium. For the necessary rubidium and caesium material I am indebted to Professor H. L. Wells, who kindly placed some very pure compounds of these metals at my disposal. The pairings given in the following table were made :

	Al = 27.	V = 51.1.	Cr = 52.1.	Fe = 56.	Co = 59.	In.
23	Na	...	Na	...	...	...
39	K	K	K	K	...	...
..	NH_4	NH_4	NH_4	NH_4	...	...
85	Rb	Rb	Rb	Rb	Rb	Rb
133	Cs	Cs	Cs	Cs	Cs	Cs
204	Tl	Tl	Tl	Tl	...	

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[1] Piccini : Ztschr. anorg. Chem., 17, 355. I have obtained indications of the existence of that of potassium.

[2] Ztschr. anorg. Chem., 17, 355 ; 20, 12. Since this article was sent to press, the remaining manganese alums have also been described by Christansen, and Piccini has obtained those of rhodium.

Solubility in Water at 25°.

As a criterion of the properties of these compounds, their solubility in water at 25° was first determined. The literature contains data only upon the solubility of the compounds of aluminium[1] and vanadium[2] and all those given seem to be of more or less doubtful character, the results having in each case been obtained without the use of a thermostat. In addition to this fact, the actual temperatures chosen by different experimenters for their determinations were rarely identical; so that their results for a given degree would have to be calculated by interpolation. I have accordingly been forced to make new measurements in each case.

The determinations were made in two-ounce bottles, containing water and the finely divided salts in excess. These were placed in a digesting-bath, as described by Noyes,[3] and rapidly shaken by means of a turbine for from four to six hours. The bottles were then placed upright in the bath and the suspended salts allowed to settle for two hours. Throughout the whole time the temperature of the bath was controlled by a gas-regulator; and its variation, in the determinations used below, never exceeded ±0.2°. From 3 to 8 cc. of the supernatant solutions were then transferred by means of a pipette, the bulb of which had been warmed, to small weighing glasses, weighed, and evaporated to dryness. The amounts of the dissolved salts were then determined by heating for four hours at about 200°, at which temperature they became fully dehydrated. The accuracy of this method was first ascertained by experiments made with a variety of alums. In these a weighed quantity of the salt was dissolved in a few cubic centimeters of water, evaporated to dryness, and heated to constant weight. The water was added to ascertain whether an error would be introduced through the formation of basic salt. The following are some of these determinations:

0.4513 gram $CsCr(SO_4)_2.12H_2O$ gave 0.2858 gram anhydrous salt; calculated, 0.2869 gram.

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[1] Poggiale: Ann. chim. phys., (3), **8**, 467; Setterberg: Ann. Chem. (Liebig), **211**, 100; Mulder: Scheidekund Verhand., 1864, 91, etc.

[2] Piccini: Ztschr. anorg. Chem., **13**, 441.

[3] Ztschr. phys. Chem., **9**, 606.

0.3540 gram $CsFe(SO_4)_2.12.H_2O$ gave 0.2262 gram anhydrous salt; calculated, 0.2259 gram.

0.2264 gram $CsAl(SO_4)_2.12H_2O$ gave 0.1411 gram anhydrous salt; calculated, 0.1403 gram.

0.7814 gram $TlCr(SO_4)_2.12H_2O$ gave 0.5473 gram anhydrous salt; calculated, 0.5474 gram.

The solubility determination of the vanadium alums required great caution, owing to the readiness with which they undergo oxidation. These salts, which were made according to Piccini's directions,[1] by electrolysis, were washed by decantation with boiled water containing carbonic acid, in the vessel in which they had been recrystallized; and were then brought directly into the bottles, without having been exposed to the air for an appreciable length of time. The water used for their solution had previously been boiled and carbon dioxide led through it in the bottles. The resulting solutions were in this case analyzed by the titration of weighed quantities according to Browning's method.[2] The alums of cobalt, of which only the potassium and ammonium compounds had been described hitherto,[3] unfortunately decompose quite rapidly in solution, giving off oxygen, and determinations could therefore not be made with them. My supply of indium, also, was too small to permit a determination of any but its caesium alum. The results obtained with this compound alone, however, sufficiently indicate the rôle of indium as an alum-forming element.

The results given below are in about half the cases averages of two or more closely-agreeing determinations, and are chosen from the total number made as having been obtained under the most perfect conditions of temperature, etc. The values refer to the number of parts of salt dissolved in 1 liter of water, and in the successive tables M^{I} represents the univalent metals contained in the alums of the trivalent metal M^{III}.

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[1] Ztschr. anorg. Chem., 9, 106.

[2] *Ibid.*, 1, 158.

[3] Proc. Roy. Soc. (Edinburgh), 59, 760.

	M^I = Na.	K.	NH_4.	Tl.	Rb.	Cs.
M^{III} = *Aluminium*. *At. wt.* = *27*.						
Anhydrous salt	...	72.3	91.9	75	18.1	4.7
Hydrated "	...	138.4	191.9	117.8	31.5	7.6
M^{III} = *Vanadium*. *At. wt.* = *51.1*.						
Anhydrous salt	...	...	316.9	256	57.9	7.71[1]
Hydrated "	...	...	785	433.1	99.3	13.1
M^{III} = *Chromium*, *At. wt.* = *52*.1.						
Anhydrous salt	...	125.1	107.8	104.8	25.7	5.7
Hydrated "	...	243.9	212.1	163.8	43.4	9.4
M^{III} = *Iron*. *At. wt.* = *56*.						
Anhydrous salt	Does not exist	Basic salt separated	441.5	361.5	97.4	17.1
Hydrated "	...		1244	646.0	169.8	27.2
M^{III} = *Indium*. *At. wt.* = *114*.						
Anhydrous salt	Does not exist	Does not exist	...	...	...	75.7
Hydrated "			...	...	...	117.3

The sodium alums known dissolve in much less than their own weight of water, and were therefore unsuitable for exact determinations. A sodium alum of iron could not be obtained. With regard to the effect of the univalent metals upon the solubility, it is seen that the higher the atomic weight of an alkali metal, the less soluble is its alum with any given trivalent metal. The solubilities of both the ammonium and thallium compounds, however, lie between those of the corresponding salts of potassium and rubidium. The salt $NH_4Al(SO_4)_2.12H_2O$ forms the only exception to this rule. It is somewhat more soluble than $KAl(SO_4)_2.12H_2O$.[2] The thallium alums, furthermore, are in each case somewhat less soluble than those of ammonium.

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[1] Piccini obtains the same order for the solubility of the vanadium alums at 10°. Expressed in parts by weight of the salts dissolved in 100 parts water, his determinations are as follows:

V—K.	V—NH_4.	V—Tl.	V—Rb.	V—Cs.
198.4	39.76	11.96	2.56	0.464

[2] In Poggiale's determinations this ammonium alum was found to be less soluble than the potassium salt. His results for the latter correspond almost exactly with mine for the ammonium salt, and those for the ammonium alum with mine for that of potassium. It is probable that the coincidence is due to a false arrangement of his tables.

The key to the effect of the trivalent elements upon the solubility relations is given in the failure of any beyond vanadium to form alums with sodium, and in the decomposition of the potassium-ferric salt by water. As this would indicate, the solubilities of the alums of the successive trivalent metals with a given univalent metal increase steadily from aluminium to indium. From what one can judge through the literature, gallium alums also follow this rule being, next to those of indium, the most soluble. The chromium alums alone form an exception. Their behavior will be touched upon at a later point.

In the following table I give the solubilities of all the alums determined, expressed in gram-molecules of the anhydrous salts per liter :

M^I.	K.	NH_4.	Tl.	Rb.	Cs.
M^{III} = Al	0.28	0.387	0.177	0.059	0.013
V	...	1.210	0.573	0.177	0.0204
Cr	0.441	0.407	0.212	0.078	0.0151
Fe	...	1.659	0.799	0.293	0.045
In	...	...	...	...	0.172

These results may be represented graphically as a function either of the molecular weight of the respective alums of given trivalent metals, which is virtually the same thing as if they were plotted according to the atomic weights of the univalent metals, but introduces the ammonium salts; or they may be referred to the atomic weights of the trivalent metals. To show the influence of both the univalent and trivalent metals, I give in Figs. I and II the results obtained by each method. In Fig. I the solubilities are plotted as functions of the molecular weights, the univalent metal being the variable. Each broken line, therefore shows the relation between the solubilities of the alums of a given trivalent metal.

As is seen, the curves are in general of the same nature, but they have no uniformity of position, and render no gradation in the solubilities of the alums visible. This is true whether we include the ammonium salts or not, or in other words, whether the solubilities be referred to the molecular weights or to the atomic weights of the univalent metals.

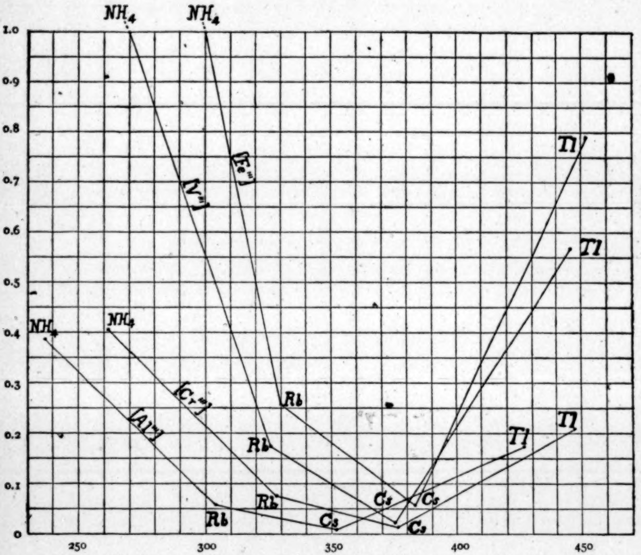

Fig. I.—Abscissae = molecular weights; Ordinates = gram-molecules per liter.

The only influence which the univalent metals or radicals exert is a specific one. The caesium salts are in all cases the least soluble, the rubidium salts next, but the comparatively great solubility of the thallous compounds—which, according to the gradations observed in the case of the compounds of the alkali metals proper, should be the least soluble of all—prevents any satisfactory representation of the solubilities as a function of the atomic weights of the univalent metals.

This specific influence of the univalent metals is readily seen in Fig. II, in which the solubilities are plotted as a function of the atomic weights of the trivalent metals.

As we pass from the caesium compounds through those of rubidium and thallium to the ammonium alums, the difference

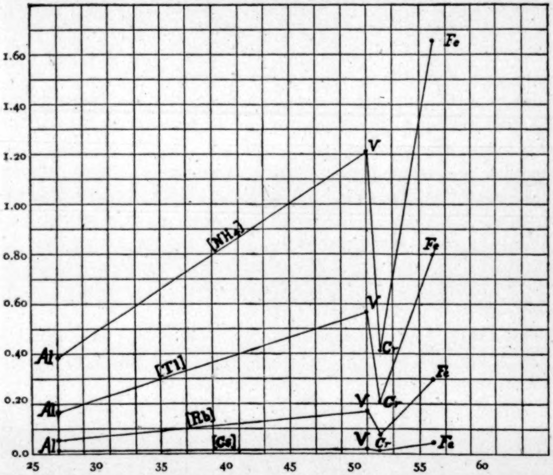

Fig. II.—Abscissae represent atomic weights, ordinates solubilities, expressed in gram-molecules per liter of water. The symbols in brackets indicate in each case the univalent metallic constituent of the alum. Each curve therefore shows the relation between the alums of a given univalent metal with the different trivalent metals

in solubility of the successive salts of a given trivalent metal becomes greater. The increase is also the greater, the heavier the trivalent metal; the result being that while the caesium alums of all the trivalent metals differ only slightly in solubility, and their curve has, therefore, a nearly horizontal position, the curves of the remaining univalent radicals successively become more inclined,[1] the whole effect being somewhat that of an opening fan. But in each case the curves show a sharp break at the chromic compounds; slight in the caesium curve, but more pronounced with each successive univalent metal. Apparently, since the chromic salts accordingly fail to fall properly within the series of gradations with increasing atomic weight of the trivalent metal, the conclusion might be drawn that the great readiness with which this element forms alums is actually an abnormal property. I believe, however, that this is a very loose way of interpreting the fact. Abnormal things do not occur in nature. In the increasing solubility of the chromic alums, as we pass from caesium to ammonium, they show exactly the same mutual relations as are shown by the alums of aluminium, vanadium, or iron. They are perfectly normal in everything except that their behavior is not expressed, like that of the other trivalent metals, by the atomic weight of the metal they contain. And this fact indicates almost positively that *the properties of the compounds are not a function of the atomic weight of the element.* If they were, chromic alums would have about twice their actual solubility.

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[1] Prof. Horace L. Wells suggests to me that the marked difference shown here between the solubilities of the rubidium and caesium alums of iron might have a practical bearing upon the technical separation of rubidium and caesium. At present this is usually effected by the fractional crystallization of their aluminium alums. By using the ferric compounds it would probably be much more perfect.

I do not mean by this to make a sweeping denial of all analogy shown in the Periodic System. Whatever the determining cause of the properties of compounds may be, it is certainly commensurable, in a great many instances, with the atomic weights. But our progress toward the systemization of the compounds will be slow indeed, if we refuse to recognize that Mendeléeff's Law is but a slight approximation of the truth. The abnormal behavior of the thallium alums, according to the Periodic System, might be conventionally explained by the position of thallium as not being a member of the first family of the table ; but in the case of chromium such an explanation is totally inapplicable. The elements aluminium, vanadium, iron, and cobalt[1] constitute members of three different families, and, nevertheless, their alums show a satisfactory gradation according to the atomic weights of these elements. Their alums are merely intermediate members in the series of which the end members, the aluminium, gallium, and indium salts, are so conspicuous because they are compounds of three elements in the same family in the system and thus exhibit the gradations required by the latter.

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[1] The effect of this element upon its alums is shown by their melting-points, as will be described later.

The chromic alums, the thallous alums, and the ammonium alums, respectively, exhibit in each case the same peculiar relations to one another as do the alums of their kindred elements with normal behavior. In the case of the ammonium alums this is especially important, for it shows that whatever the determining cause of the properties of the alums may be, *exactly the same cause must be ascribed to the behavior of the ammonium salts as to that of the alums containing only metals;* and since the ammonium radical has no true atomic weight, therefore, that the atomic weight itself is not the determining cause in the case of any alums whatsoever.

It is an interesting fact that the molecular volumes of the alums, when arranged according to their ascending values, bring both the trivalent and univalent elements into the same order as do their solubilities. In the following tables[1] the molecular volumes are given as calculated from Soret's determinations, with the double formulas, $M^I_2SO_4.M^{III}_2(SO_4)^3.24H_2O$ as the basis of the molecular weights. The solubilities are expressed in gram-molecules per liter:

	$M^{III} = Al.$		$M^{III} = Cr.$		$M^{III} = Fe.$	
	Molecular volume.	Solubility.	Molecular volume.	Solubility.	Molecular volume.	Solubility.
$M^I = K$	546.9	0.28	550.8	0.441	....	....
NH_4	555.9	0.387	557.6	0.407	562.8	1.659
Tl	566.6	0.177	557.7	0.212	560.2	0.799
Rb	562.2	0.059	561.7	0.079	573.3	0.293
Cs	579.2	0.013	581.8	0.015	579.3	0.045

	$M^I = Cs.$		$M^I = (NH_4).$	
	Molecular volume.	Solubility.	Molecular volume.	Solubility.
$M^{III} = Al$	578	0.013	555.9	0.387
Cr	582	0.015	557.6	0.407
Fe	579	0.045	562.8	1.659
In	584	0.172	....	....

The coincidence, while not absolute, shows that there is a close connection between the molecular volumes of the alums and their solubility. The variations, furthermore, lose much in weight in the fact that a very small error in the determination of the specific gravity is greatly multiplied in the quotient

$$\frac{\text{molecular weight}}{\text{specific gravity}}.$$

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[1] Soret: Arch. sc. phys. Nat. (Genève), (3), **12**, 553, etc.; Arzruni: Physikalische Chemie der Krystalle (1893), p. 130. Soret's original article is not at my disposal.

Solubility at Different Temperature.—The next question to be decided was whether there is any regularity in the effect of increasing temperature upon the solubility of different alums. Here I was much limited in my choice of salts, inasmuch as the ferric compounds break down into basic salts when treated with pure water at higher temperatures, and the chromic compounds pass into their green modifications at about 50°. This behavior of the ferric alums prevented the comparative study of any but the rubidium and caesium compounds. As I wished merely to find the general direction of the solubility curves, I did not carry out determinations at temperatures below 25°. Experiments on chromic salts showed that even at 45° they became slightly green on prolonged digestion, and 40° was therefore taken as the upper limit. The following table gives the solubilities of the rubidium and caesium alums of aluminium, chromium, and iron, at intervals of 5° between these limits :

	Rb-Al.		Rb-Cr.		Rb-Fe.	
	Parts per liter.	Gram-mol. per liter.	Parts per liter.	Gram-mol. per liter.	Parts per liter.	Gram-mol. per liter.
25°	18.1	0.059	25.7	0.079	97.4	0.294
30°	21.9	0.072	31.7	0.096	202.4	0.617
35°	26.6	0.087	41.1	0.128	....[1]	....
40°	32.2	0.106	59.7	0.181	....	....
	Cs-Al.		Cs-Cr.		Cs-Fe.	
25°	4.7	0.013	5.7	0.015	17.1	0.045
30°	5.89	0.0167	9.6	0.025	25.2	0.066
35°	7.29	0.0207	12.06	0.032	37.5	0.099
40°	9.00	0.0256	15.3	0.0405	60.4	0.156

Fig. III shows the curves corresponding to the solubilities of these salts expressed in gram-molecules per liter. To facilitate comparison, the solubility curves of the rubidium salts are dotted.

There seems here to be no marked connection between the various alums with respect to the univalent metals, the curve of $CsFe(SO_4)_2$ crossing that of $RbAl(SO_4)_2$ at about 34°. But if we compare the alums, first of caesium, and then of rubidium, we see that the more soluble the alum of a given

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[1] Basic salt formed.

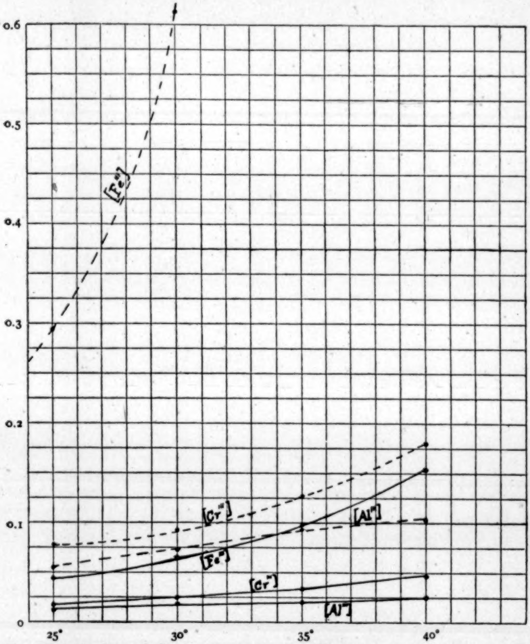

Fig. III.—Abscissae indicate temperatures, ordinates gram-molecules per liter. Symbols in brackets indicate in each case the trivalent metallic constituent of the alum. Curves of rubidium salts are dotted, those of caesium salts solid.

univalent metal is at 25°, the more rapidly does its solubility increase with the temperature. This is marked even in the case of the caesium salts of aluminium and chromium, the solubilities of which at 25° are almost the same (0.013 and 0.015 gram-mol.). The curve of $RbFe(SO_4)_2$ could be followed only to 30°, as at 35° a sparingly soluble basic salt separated from the solution; and the extreme difference in solubility shown for the interval 25° to 30°, may in part be ascribed to a hydrolytic action.

Melting-points.—The melting-point of a hydrated salt is, of course, intimately connected with its solubility, so that in studying them one would expect results approximately analogous to the above. But at the same time I was enabled, in this way, to examine a greater variety of alums, including those of cobalt, the solubility of which could not be determined, the rubidium-indium salt, and the potassium-vanadium and potassium-ferric compounds.

The cobaltic salts examined were those containing rubidium and caesium. These were made in the same way as Marshall[1] obtained the ammonium and potassium cobaltic alums, by the electrolytic oxidation of cobaltous sulphate and addition of the calculated amount of the salts of the desired alkali metal. Both compounds came down in coarse crystalline grains, which could be readily washed by lixiviation with cold water. They were sufficiently stable to permit of rapid drying in the air, but on standing for any length of time they lost oxygen and yielded cobaltous sulphate. The rubidium alum decomposed in this manner, even in a sealed specimen-tube, on standing for a few months. The caesium compound, however, when preserved in the same way, has still retained its green color, thus forming an interesting example of the greater stability of caesium double salts over those of rubidium. Both compounds crystallized in glistening microscopic octahedrons. In view of their marked physical properties, it was not deemed necessary to submit them to a full analysis, but as a matter of general precaution, a weighed quantity of each was ignited below a red heat and the amount of the residual cobaltous and alkali sulphates determined.

0.0683 gram $RbCo(SO_4)_2.12H_2O$ gave 0.0361 gram $Rb_2SO_4 + CoSO_4$; calculated, 0.0357 gram.

0.7004 gram $CsCO(SO_4)_2.12H_2O$ gave 0.2962 gram $Cs_2SO_4 + CoSO_4$; calculated, 0.2959 gram.

The determination of the melting-points was carried out in sealed capillary tubes, of various diameters, and about 2 inches in length. The tubes were in each case filled to somewhat over half their height with the powdered salts. At least five determinations were made with each compound, and samples from several different preparations used for each. Variations in the manner of heating, etc., introduce comparatively large errors in the melting-points, which are in no case very sharp. But after some practice I was able, by carefully following one method of procedure, to reduce the error to about 1°; and in cases where two alums melted at about the same point, as the NH_4–Al(95°) and NH_4–Cr(94°) salts, comparative determinations were made side by side in the same experiment. So, while I make no pretence to great accuracy in these determinations, the errors involved are at least about the same for each compound, and thus the data given below are not vitiated for the purpose of comparison.

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[1] Proc. Roy. Soc. (Edinburgh), 59, 760.

The literature contains various notices on the melting-points of aluminium and chromium alums, and Piccini also determined approximately those of the vanadium salts with sodium (9°), potassium (20°), and ammonium (50°). The last I find to melt at 45°, and for vanadium-potassium alum I have obtained data anywhere from 20° to 28°. The purification of this compound is so difficult that a constant melting-point cannot be observed. My results on the aluminium alums correspond fairly well with those of Erdmann,[1] though being slightly higher, and both his and mine are much higher than those determined by Tilden.[2]

	Na–Al.	K–Al.	NH_4–Al.	Rb–Al.	Cs–Al.
Tilden	61	84°.5	92°	99°	106°
Erdmann	—	92°.5	—	105°	120°.5
Locke	63	91°	95°	109°	122°

Observations on sodium-chromium and caesium-indium alums gave no satisfactory results, the fusion process in each case covering a range of about 10°, and in the case of the indium salt being even then imperfect. My complete results follow:

	M^{III} = Al.	V.	Cr.	Fe.	Co.	In.
M^I = Na	63°	(9°)[3]	..	..	..	..
K	91°	(20°)[3]	89°	28°	..	..
Tl	91°	48°	92°	37°	..	..
NH_4	95°	45°	94°	40°	..	(36°)[4]
Rb	109°	64°	107°	53°	47°	42°
Cs	122°	82°	116°	71°	63°	..

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[1] Arch. Pharm., **232**, 3.

[2] J. Chem. Soc., **45**, 266.

[3] Piccini: *Loc. cit.*

[4] J. prakt. Chem., [2], **7**, 14.

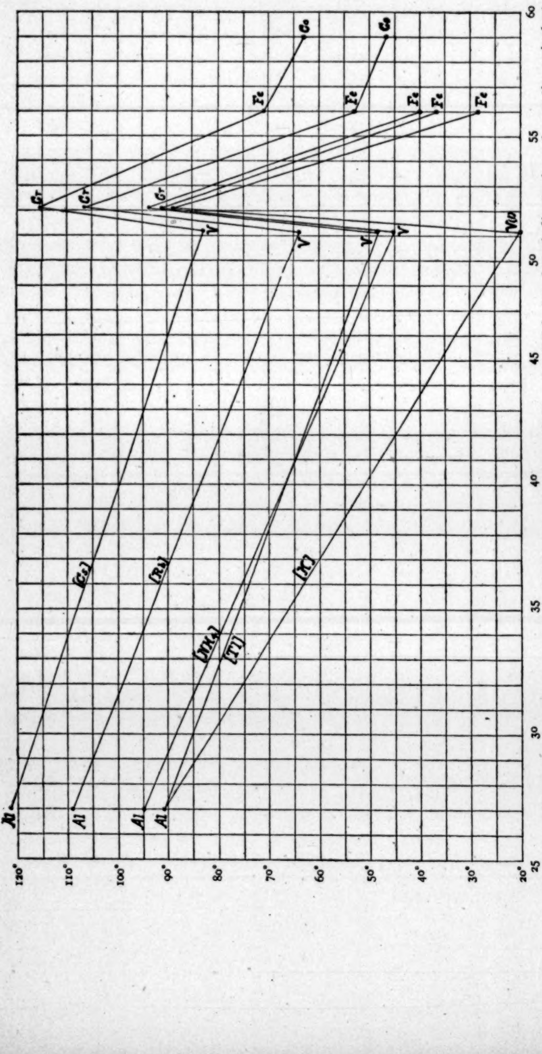

Fig. IV.—Ordinates represent temperatures; abscissae, molecular weights. Symbol in brackets indicates in each case the univalent metallic constituent of the alum.

The order in which the trivalent metals fall, according to the melting-points of their alums with a given univalent metal, is here the same as when determined by the solubility-relations of their salts. The one exception lies in the doubtful melting-point of vanadium-potassium alum, which is a few degrees lower than that of the corresponding ferric salt. The cobalt alums melt at a slightly lower temperature than do the iron compounds, and indium-rubidium alum lower than any other of the rubidium salts, just as the indium-caesium alum is the most soluble member of the caesium series.

With reference to the univalent metals, however, we find the same order as in the solubility tables, so far as the alkali metals are concerned. But the order of the thallium and ammonium series is changed, the thallium salts lying next those of potassium. The vanadium compounds here form the only exception, and in view of their great instability it is to be doubted whether this is not due to unavoidable impurities.

In Fig IV I give the melting-points plotted as a function of the atomic weights of the trivalent metals, R^{III}.

Here, again, we see a sharp break in the case of the chromic salts. The melting-points of the caesium and rubidium alums of aluminium, vanadium, iron, and cobalt are represented by nearly parallel straight lines, which would indicate a very simple relation between them and the atomic weights of these metals. But we must either admit that the values of the melting-points do not depend upon the atomic weights, or that the chromic alums form an exception to a law of nature.

LXXIX.—ON ACETYL AND BENZOYLIMIDODITHIOCARBONIC ESTERS.

By Henry L. Wheeler and Treat B. Johnson.

It has been found in general that, when a thiourethane of the structure —NHCS.OR[1] or —NHCS.SR[2] is treated with alkali and an alkyl halide, imidothiocarbonic esters result.

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[1] Liebermann: Ann. Chem. (Liebig), **207**, 141 (1881); Wheeler, Barnes, Johnson, and Dustin: This Journal, **24**, 60; *Ibid.*, 189; *Ibid.*, 424 (1900).

[2] Fromm and Block: Ber. d. chem. Ges., **32**, 2210 (1899); Busch and Lingenbrink: *Ibid.*, 2620.

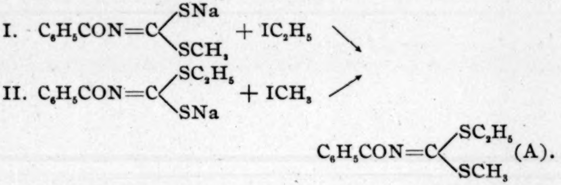
The acyldithiocarbamates form no exception to this rule, although Chaularoff[1] states that he was unable to introduce the ethyl group into ethyl acetyldithiocarbamate,

$$CH_3CONHCS.SC_2H_5,$$

by means of the silver salt and ethyl iodide.

In a previous paper from this laboratory it was shown that, if the urethane is dissolved in alcohol containing sodium ethylate and then treated with ethyl iodide, a good yield of the acylimidodithiocarbonic ester is obtained. This method has now been employed for the preparation of numerous analogues.

Our chief object in examining these compounds has been to determine whether stereochemical isomers are formed when esters with unlike groups are prepared by different methods. For example, methyl ethylbenzoylimidodithiocarbonate (A) might exhibit this sort of isomerism when obtained from sodium methylbenzoylimidodithiocarbonate and ethyl iodide (I) on the one hand, and from sodium ethylbenzoylimidodithiocarbonate and methyl iodide on the other (II).

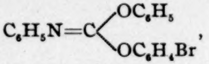


$$\text{I.}\quad C_6H_5CON{=}C\begin{cases}SNa\\SCH_3\end{cases} + IC_2H_5 \searrow$$

$$\text{II.}\quad C_6H_5CON{=}C\begin{cases}SC_2H_5\\SNa\end{cases} + ICH_3 \nearrow$$

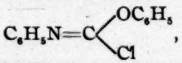
$$C_6H_5CON{=}C\begin{cases}SC_2H_5\\SCH_3\end{cases}\ \text{(A).}$$

A similar question in the oxygen series has already been decided in the negative by Hantzsch and Mai.[2] They showed that phenyl *p*-bromphenylphenylimidocarbonate,



$$C_6H_5N{=}C\begin{cases}OC_6H_5\\OC_6H_4Br\end{cases},$$

whether prepared from the chloride



$$C_6H_5N{=}C\begin{cases}OC_6H_5\\Cl\end{cases},$$

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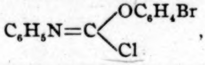
[1] Ber. d. chem. Ges., **15**, 1987 (1882).

[2] *Ibid.*, **28**, 977 (1895).

and sodium *p*-bromphenolate, or from the chloride,



$$C_6H_5N{=}C\begin{cases}OC_6H_4Br\\Cl\end{cases},$$

and sodium phenolate turns out to be one and the same compound.

It was stated by Fromm and Block[1] that they intended to examine this question in the imidodithiocarbonic ester series, but later, in answer to a private communication, Prof. Fromm very kindly replied that he did not wish to reserve this subject for himself, and that, owing to press of other work, he would be very glad to have the question taken up by others.[2]

In order to obtain an idea of the properties of this new class of compounds we first examined a number with simple alkyl groups, and found that, with the exception of dimethylbenzoylimidodithiocarbonate, the lower members of series are oils.

Methyl ethylbenzoylimidothiocarbonate (A, above), prepared in the two ways, proved to be an oil which distilled unaltered at 224° at 20° mm. pressure. No appreciable difference in boiling-point could be detected in the two samples. However, in this case it was possible that in heating one form had been converted into another.

Our efforts were then directed towards obtaining esters that are solid at ordinary temperatures, and many unexpected difficulties were encountered before the desired results were obtained. An account of these difficulties and of experiments in which we obtained mostly degative results, is given here in considerable detail, since it serves to illustrate some peculiar properties of the acyldithiocarbamates or of the acylimidodithiocarbonic esters.

We found that although the dimethyl and dibenzyl imido esters are solids, the methyl benzyl product, prepared in either way, in alcoholic solutions, is an oil which decomposes on distilling at reduced pressure.

When groups with higher molecular weights were selected, we met with a number of cases where solids were obtained but where the desired ester could be prepared in only one way.

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[1] Ber. d. chem. Ges., 32, 2212 (1899).

[2] Since the above was written Busch has described some samples of stereochemical isomerism in the case of hydrazones of the dithiocarbonic esters. Ber. d. chem. Ges., 34, 1119 (1901).

The reaction took place smoothly and gave well crystallized products, which could be easily purified, when ethyl chloracetate and paranitrobenzyl chloride were allowed to act on benzylbenzoyldithiourethane, in the presence of sodium ethylate. On the other hand, under precisely similar conditions, the action of benzyl chloride on benzoyldithiourethaneethylacetate, $C_6H_5CO.NHCS.SCH_2CO_2C_2H_5$, and on parabrombenzylbenzoyldithiourethane, and on paranitrobenzylbenzoyldithiourethane, gave oils which in the first two cases showed no signs of crystallizing after standing for weeks.

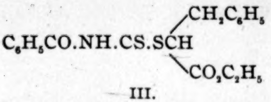
Benzoyl chloride reacted easily and quantitatively with phthalimidoethylbenzoyldithiocarbonate,

$$C_6H_5CO.NHCS.SCH_2.CH_2N(CO)_2C_6H_4\ ;$$

but no reaction, in the cold, could be obtained from the sodium salt of benzylbenzoyldithiocarbamate and bromethylphthalimide. When the mixture was heated the sodium salt was decomposed.

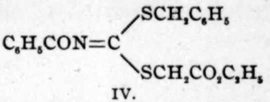
Some of those urethanes which did not act smoothly with benzyl chloride also failed to give the corresponding esters with like groups. It therefore appeared that the difficulty, in these cases, was to be explained by the fact that sodium ethylate decomposed the urethanes (see below).

An attempt was then made to obtain a solid by shaking the aqueous alkaline solution of benzoyldithiourethane ethyl acetate with benzyl chloride. This, in fact, gave a solid which proved to be a sodium salt of a compound structurally isomeric with the product prepared from ethyl chloracetate and benzylbenzoyldithiourethane in sodium ethylate solutions. When this was suspended in water and treated with carbonic acid, a bright-yellow compound was obtained. Although this had precisely the same melting-point as its isomer it was decidedly different in other respects. The bright-yellow color, its solubility in alkali, and the fact that the ester prepared in the other way gave no sodium salt, showed that we had to deal here with a dithiourethane, III, and not an imidocarbonic ester, IV :



$$C_6H_5CO.NH.CS.SCH\begin{array}{l}\diagup CH_2C_6H_5\\ \diagdown CO_2C_2H_5\end{array}$$

III.



$$C_6H_5CON{=}C\begin{array}{l}\diagup SCH_2C_6H_5\\ \diagdown SCH_2CO_2C_2H_5\end{array}$$

IV.

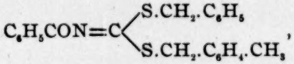
This peculiar result suggests that the methylene hydrogen in compounds containing the complex —S—CH_2CO— will be found to undergo substitution similar to that in desoxybenzoin and benzyl cyanide, although Loven[1] states that he was unable to introduce the methyl group into thiodiglycollic ester by means of sodium alcoholate and methyl iodide. We hope to examine this question later.

It was found that benzylbenzoyldithiourethane forms a fairly stable sodium salt, and from this the dibenzyl carbonic ester, which is characterized by its relatively high melting-point, can be quantitatively obtained. We therefore sought for radicals closely similar to benzyl, and, on employing the metaxyl and mesityl groups, we were finally successful in obtaining solid imidoesters by the two different ways.

Benzylbenzoyldithiocarbonate, sodium ethylate, and metaxylyl bromide reacted in a few minutes and gave a product melting at 97° to 98°.

Metaxylylbenzoyldithiocarbamate, sodium ethylate, and benzoyl chloride reacted after about twelve hours, and gave a product melting mostly at 85° to 86°, but the material did not become clear until 89°.5, and repeated crystallization did not alter this melting-point.

If, instead of using sodium ethylate solutions, the reactions were carried out, in both cases, by shaking in aqueous alkali, the metaxylyl benzylbenzoylimidodithiocarbonic ester,



$$C_6H_5CON{=}C\begin{array}{l}\diagup S.CH_2.C_6H_5\\ \diagdown S.CH_2.C_6H_4.CH_3\end{array},$$

obtained melted precisely at 97° to 98° and the products formed by the two different methhods were identical in every respect.

Although metaxylyl benzoyldithiocarbamate and sodium ethylate do not react smoothly with benzyl chloride, nevertheless with metaxylyl bromide they react in a perfectly smooth manner.

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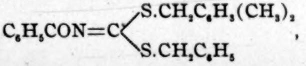
[1] Ber. d. chem. Ges., **18**, 3242 (1885).

That the above ester, melting at 85° to 89.°5, contains some impurity or decomposition-product which cannot be separated by crystallizing from alcohol, appears probable, not only from its melting-point but also from the behavior of mesitylbenzoyldithiourethane towards benzyl chloride. It is a curious fact that these substances, in alcoholic solutions, show little tendency to form an imido ester. One-half of the urethane can be recovered unaltered from the alkaline solution after standing twelve hours, the other half is decomposed.

Vol. 2
1901

If, instead of using alcoholic solutions, the mesityl urethane is shaken with benzyl chloride and aqueous alkali, the substances react with remarkable ease, the reaction is complete in a few minutes, and the resulting mesityl benzyl ester of benzoylimidodithiocarbonic acid,



$$C_6H_5CON{=}C\!\left\langle\begin{array}{l}S.CH_2C_6H_3(CH_3)_2\\S.CH_2C_6H_5\end{array}\right.,$$

melts at 117°.5.

On the other hand, a product identical with this is readily obtained from mesityl bromide, benzylbenzoyldithiourethane and sodium ethylate. These substances react immediately and in a perfectly smooth manner in alcoholic solution.

A somewhat similar difference in tendency to react in alcoholic solutions was observed in the preparation of an imido ester from ethyl α-benzoyldithiourethane propionate, $C_6H_5CO.NHCS.SCH(CH_3)CO_2C_2H_5$, and benzyl chloride, in which case the action was not smooth, while, when prepared in the other manner, from methyl α-brompropionate and benzylbenzoyldithiourethane, a smooth reaction was obtained.

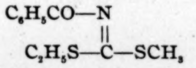
Every reactive halogen compound that has been tried with benzylbenzoyldithiourethane reacts smoothly, while the difficulties encountered in the use of sodium ethylate solutions have been confined entirely to other urethanes. This would indicate that the benzyl urethane is the only one examined that is not decomposed, to some extent, by treating with sodium ethylate. This decomposition of the urethanes will

. 26
901

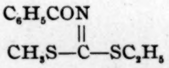
explain most of the negative results, but an explanation for the relative inertness of the urethanes towards benzyl chloride in the presence of sodium ethylate is lacking.

The results show, however, that stereoisomeric acylimidodithiocarbonic esters do not result by the methods in question.

When the acylimidodithiocarbonic esters are treated with amines, mercaptan is evolved, even in the cold, and acylpseudothioureas are smoothly formed. No pseudothioureas of this type have been described, and since they have proved to be quite reactive compounds they will form the subject of a later paper. It is perhaps of interest to note here that when the esters with unlike alkyl groups are treated with aniline, etc., the product obtained is a mixture of two acylpseudothioureas and that both alkyl groups are partially separated as mercaptan. This is not what would be expected if the acylimidodithiocarbonic esters corresponded to a single stable one of the following stereochemical modifications:



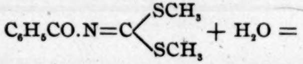
$$\begin{array}{c} C_6H_5CO\text{—}N \\ \| \\ C_2H_5S\text{—}C\text{—}SCH_3 \end{array}$$



$$\begin{array}{c} C_6H_5CON \\ \| \\ CH_3S\text{—}C\text{—}SC_2H_5 \end{array}$$

It appears more probable that the esters in question, consist of mixtures of these two forms.

The behavior of the esters with hydrochloric acid is also in accordance with this view. The symmetrical esters, when gently warmed with acid, undergo hydrolysis and are converted into acylthiolcarbamic esters, as follows:

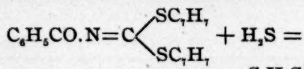


$$C_6H_5CO.N{=}C\begin{cases} SCH_3 \\ SCH_3 \end{cases} + H_2O =$$

$$C_6H_5CO.NHCO.SCH_3 + HSCH_3.$$

Ethyl benzylbenzoylimidodithiocarbonic ester gave a mixture of the two possible thiolcarbamic esters.

When the acylimidodithiocarbonic esters are heated in a stream of dry hydrogen sulphide, mercaptan is given off and the esters are converted into acyldithiocarbamates:



$$C_6H_5CO.N{=}C\begin{cases} SC_7H_7 \\ SC_7H_7 \end{cases} + H_2S =$$

$$C_6H_5CO.NHCS.S.C_7H_7 + C_7H_7SH.$$

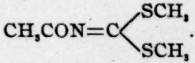
EXPERIMENTAL PART.

Preparation of Acyldithiourethanes.—Most of the primary monothiocyanates unite directly with thiol acids when warmed in benzene solution. As a rule, secondary thiocyanates react less smoothly and many give no dithiourethanes but form products containing sulphur and no nitrogen; 1′-thiocyanethylbenzene, $C_6H_5CH(SCN)CH_3$, and thiocyandesoxybenzoin, $C_6H_5CO—CH(SCN)C_6H_5$, for example. The investigation of the behavior of secondary and tertiary thiocyanates $>$CHSCN and $\equiv$C—SCN with thiol acids is now in progress in this laboratory.

Preparation of Acylimidodithiocarbonic Esters.—In all our experiments the action of sodium ethylate and alkyl halide on the dithiourethanes, at ordinary temperatures and in alcoholic solution, was first tried. When this process gave oils or when a satisfactory reaction was not obtained, the urethanes were dissolved in aqueous alkali and shaken with the halides. In most cases the action of alkali, and especially that of sodium alcoholate, produces a partial decomposition according to the following:

$$C_6H_5CONC(SNa)SR = C_6H_5COSNa + NCSR.$$

This appears to be the chief reaction when the urethanes are treated with sodium in benzene. The acylimidodithiocarbonic ester is then obtained mixed with a thiol ester of benzoic acid and a sulphocyanide, and the sulphocyanide further decomposes into sodium cyanide and a disulphide. Besides this, when sodium alcoholate is used and the formation of imido esters slowly takes place, the latter are partially decomposed with the result that mercaptan is formed which in certain cases also tends to contaminate the products.

Dimethylacetylimidodithiocarbonate, 

$$CH_3CON{=}C\begin{cases}SCH_3\\SCH_3\end{cases}$$

.—This, the first member of the series, was prepared from sodium methyl acetylimidodithiocarbonate and methyl iodide in alcoholic solution. After standing for twelve hours, water precipitated a pale-yellow oil which, when washed and dried, was distilled at 20 mm. pressure. About one-half of the oil boiled below 135°(methyl rhodanide and methyl thiolbenzoate), then the remainder distilled at 135° to 145°. On redistilling, at the same pressure, it practically all boiled at 142° to 144°, and a nitrogen determination in the latter portion of this was made with the following result:

	Calculated for $C_5H_9ONS_2$.	Found.
N	8.58	8.34

Diethyl acetylimidodithiocarbonate was described in a previous paper.[1]

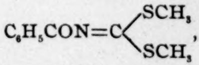
Isoamyl acetyldithiocarbamate, $CH_3CO.NHCS.SC_5H_{11}$.—Isoamyl thiocyanate did not combine as smoothly as the lower rhodanides with thioacetic acid. A portion of the reaction-product solidified, and on crystallizing this from alcohol yellow plates were obtained which melted constantly at 84°. A nitrogen determination gave:

	Calculated for $C_8H_{15}ONS_2$.	Found.
N	6.8	7.0

When this was dissolved in alcoholic sodium ethylate and treated with isoamyl bromide an oil was obtained, about one-half of which boiled below 192° at 20 mm. pressure, (isoamyl thiolacetate and amyl thiocyanate), the remainder distilled at 192° to 205°. On redistilling, at the same pressure, a portion was collected boiling at 198° to 200°. The analysis of this agreed with the calculated percentage for diisoamyl acetylimidodithiocarbonate.

	Calculated for $C_{13}H_{25}ONS_2$.	Found.
N	5.09	5.39

Dimethyl benzoylimidodithiocarbonate,



$$C_6H_5CON{=}C\begin{cases}SCH_3\\SCH_3\end{cases},$$

previously described, and concentrated hydrochloric acid react almost at once. The ester does not dissolve but mercaptan is evolved, and on crystallizing the product from 95 per cent alcohol, colorless needle-like prisms results, which melt at 153° to 154°. When this was mixed with the product which we obtained by heating methyl benzoylthioncarbamate with methyl iodide[1] the melting-point was not altered. The substance is therefore methyl benzoylthiolcarbamate, $C_6H_5CO.NHCO.SCH_3$.

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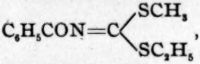
[1] Wheeler and Merriam: *Loc. cit.*

Diethyl benzoylimidodithiocarbonate and hydrochloric acid acted in a similar manner. The product from alcohol melted at 108° and was identical with ethyl benzoylthiolcarbamate, $C_6H_5CO.NHCO.SC_2H_5$, which we obtained from the corresponding diethyl monothiocarbonate and hydrochloric acid.[2]

Methyl ethyl benzoylimidodithiocarbonate,



$$C_6H_5CON{=}C\begin{cases}SCH_3\\SC_2H_5\end{cases}$$

, was prepared from ethyl benzoylimidodithiocarbonate, sodium ethylate and methyl iodide. On distilling the pale yellow-colored oil thus obtained at 20 mm. pressure, it practically all boiled at 224° to 225°.5. Eight grams of the oil were obtained from 13 grams of the urethane. A nitrogen determination gave :

	Calculated for $C_{11}H_{13}ONS_2$.	Found.
N	5.86	6.18

Apparently this same oil was obtained when methyl benzoylimidodithiocarbonate, sodium ethylate, and ethyl iodide were allowed to react. The product in this case boiled at 222° to 224°, the chief quantity boiling sharply at 224° at 20 mm. pressure. When this sample was treated with concentrated hydrochloric acid it readily reacted, but the product, on crystallizing from alcohol, acted like a mixture. It melted at about 120° to 145°, and three crystallizations failed to give a definite melting-point. This material probably consisted of a mixture of the above methyl and ethyl benzoylthiolcarbamates.

When methyl ethyl benzoylimidodithiocarbonate was warmed with aniline a reaction started immediately. The escaping gas was passed into a cooled receiver, and thence into a solution of mercuric cyanide. The oil which condensed in the receiver gave a yellow precipitate with mercuric cyanide, which melted at 66° to 70°. This, therefore, was ethyl mercaptide. The gas which passed into the mercuric cyanide solution produced a grayish precipitate which was difficultly soluble in alcohol and melted at 169° to 170°. This was, therefore, methyl mercaptide.

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[1] This JOURNAL, 24, 201.

[2] *Loc. cit.*

The solid product of the reaction was crystallized repeatedly from alcohol, whereupon it separated in the form of flattened prisms and melted constantly at 79° to 80°. A nitrogen determination gave :

	Calculated for $C_6H_5CO.N{=}C(SCH_3)NHC_6H_5$.	Calculated for $C_6H_5CO.N{=}C(SC_2H_5)NHC_6H_5$.	Found.
N	10.37	9.86	10.42

The above two acylpseudothioureas were described by Wheeler and Merriam.[1] The product of the action of aniline on dimethyl benzoylimidodithiocarbonate melted at 104°, while that from the diethyl ester melted at 88°. Since the material in the present case is not identical with either of these, and since both methyl and ethyl mercaptan were evolved in its preparation, it follows that this product is a mixture of the two pseudothioureas, which cannot be separated by crystallizing from alcohol. Similar results were obtained by the action of alcoholic ammonia. The product had no definite melting-point and behaved like a mixture.

Di-n-propyl benzoylimidodithiocarbonate, $C_6H_5CO.N{=}CS(C_3H_7)_2$, was obtained as a pale-yellow oil which boiled at 238° to 239° at 20 mm. pressure and a nitrogen determination, for which we are indebted to Mr. J. G. Wild, gave :

	Calculated for $C_{14}H_{19}ONS_2$.	Found.
N	5.01	5.40

Isoamyl benzoyldithiocarbamate, $C_6H_5CONHCS.SC_5H_{11}$.—When molecular quantities of amyl sulphocyanide and thiobenzoic acid were warmed on the steam-bath for twenty-four hours, a thick red oil was obtained which slowly solidified on standing. On crystallizing from dilute alcohol it was obtained in the form of yellow prisms and melted at 48° to 49°.

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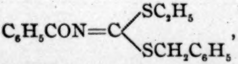
[1] *Loc. cit.*

We are indebted to Mr. W. M. Clark for the following nitrogen determination:

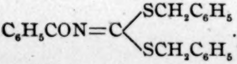
	Calculated for $C_{13}H_{17}ONS_2$.	Found.
N	5.25	5.79

Ethyl benzyl benzoylimidodithiocarbonate,



$C_6H_5CON{=}C\begin{cases}SC_2H_5\\SCH_2C_6H_5\end{cases}$, when prepared from the ethyl or benzyldithiourethane, in alcoholic solution, proved to be an oil which could be neither solidified nor distilled without decomposition. The same result was obtained when ethyl benzoyldithiocarbamate was shaken with aqueous alkali and benzyl chloride. Isoamyl benzyl benzoylimidodithiocarbonate prepared from the above isoamyl benzoyldithiourethane showed no signs of crystallizing after standing for several weeks.

Dibenzyl benzoylimidodithiocarbonate,



$C_6H_5CON{=}C\begin{cases}SCH_2C_6H_5\\SCH_2C_6H_5\end{cases}$.—When 42 grams of benzyl benzoyldithiocarbamate, 3.4 grams of sodium, in 150 cc. of alcohol and 18.5 grams of benzyl chloride were mixed, a reaction took place almost immediately and the material became semisolid, from the separation of a mass of colorless needles. The reaction was very smooth. On adding water and then crystallizing from alcohol the ester separated in the form of balls of long, colorless, shining, silky needles, which melted sharply at 97° and had an odor which suggested roses or carnations. A nitrogen determination gave:

	Calculated for $C_{22}H_{19}ONS_2$.	Found.
N	3.71	3.81

Paranitrobenzyl benzoyldithiocarbamate,

$C_6H_5CO.NHCS.SCH_2C_6H_4NO_2$.—This results smoothly from the rhodanide and thiobenzoic acid, when warmed in benzene on the steam-bath. It crystallizes beautifully from alcohol in clusters of short, yellow needles, which melt at 155° to 156°. A nitrogen determination made by Mr. Clark gave:

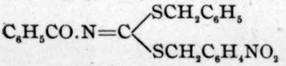
	Calculated for $C_{15}H_{12}O_3N_2S_2$.	Found.
N	8.43	8.11

Parabrombenzyl benzoyldithiocarbamate, $C_6H_5CO.NHCS.SCH_2C_6H_4Br$, prepared from the rhodanide and thiobenzoic acid, did not melt sharply on crystallizing from alcohol. It was dissolved in dilute alkali and precipitated by carbon dioxide, whereupon, on crystallizing from alcohol, it separated as a fine crystalline, yellow powder, which melted at 126°. A nitrogen determination gave:

	Calculated for $C_{15}H_{12}ONS_2Br$.	Found.
N	3.82	4.01

When this was treated with sodium ethylate and benzyl chloride nothing but an oil was obtained which did not solidify after a number of weeks.

Benzyl paranitrobenzyl benzoylimidodithiocarbonate,



$$C_6H_5CO.N{=}C\begin{cases} SCH_2C_6H_5 \\ SCH_2C_6H_4NO_2 \end{cases}$$

, when prepared from benzyl benzoyldithiocarbamate and *p*-nitrobenzyl chloride was obtained as an oil, which, after standing for three weeks, solidified. When this was crystallized from alcohol it formed short needles and melted at 84° to 85°, and a nitrogen determination gave:

	Calculated for $C_{22}H_{18}O_3N_2S_2$.	Found.
N	6.63	6.48

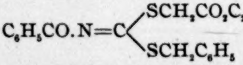
Attempts to prepare this from *p*-nitrobenzyl benzoyldithiourethane and benzyl chloride invariably resulted in the formation of an oil which refused to solidify. The difficulty here is due to the unstable nature of the sodium salt. The nitrourethane dissolves in sodium alcoholate to a deep blood-red solution, and when treated with *p*-nitrobenzyl chloride a red tar is obtained. No attempt was made to prepare this imido ester in aqueous solutions.

Ethyl Acetate Derivative of Benzoyldithiocarbamic Acid, $C_6H_5CO.NHCS.SCH_2CO_2C_2H_5$.—In another article attention was called to the fact that the rhodanethyl acetate of Claesson combines with thiobenzoic acid, smoothly and practically quantitatively, to form a yellow crystalline cake of the above dithiourethane. This substance, therefore, contrary to the statements of Frerich and Beckurts,[1] is not a mustard-oil. On crystallizing from alcohol, yellow plates are obtained melting at 128°, and a nitrogen determination, made by Mr. A. P. Beardsley, gave the following result:

	Calculated for $C_{12}H_{13}O_3NS_2$.	Found.
N	4.94	5.00

When this urethane was treated with sodium alcoholate and ethyl chloracetate an oil was obtained. This boiled at 137° to 195° at 15 to 30 mm. pressure. A considerable portion distilling at 188° to 192° at 23 mm. pressure. This oil was free from nitrogen and agreed in properties with ethyl benzoylthioglycollate, $C_6H_5CO.SCH_2CO_2C_2H_5$, which, when pure, boils at 185° to 187° at 15 mm. pressure, and when mixed with aniline forms benzanilide.

Ethyl Acetate Derivative of Benzyl benzoylimidodithiocarbonate,



$$C_6H_5CO.N{=}C\begin{cases} SCH_2CO_2C_2H_5 \\ SCH_2C_6H_5 \end{cases}$$

.—This was formed in a smooth manner when 8 grams of benzyl benzoyldithiocarbamate were dissolved in alcohol containing 0.64 gram of sodium and then 3.4 grams of ethyl chloracetate were added. On standing twelve hours water precipitated an oil, which easily solidified, and on crystallizing from strong alcohol colorless, flattened prisms, melting sharply at 79°, were obtained. Nitrogen and sulphur determinations gave the following results:

	Calculated for $C_{19}H_{19}O_3NS_2$.	Found.
N	3.75	3.63
S	17.15	17.04

Attempts to prepare this ester from the ethyl acetate derivative of benzoyldithiourethane and benzyl chloride, using sodium alcoholate in alcohol solution, were without success. A reaction soon took place and sodium chloride separated, but whether the ester was precipitated with water after an hour's standing, or longer, an oil was invariably obtained which showed no evidence of crystallizing after standing a number of weeks. It also refused to solidify in a freezing-mixture.

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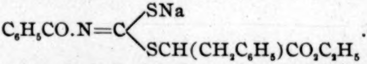
[1] Arch. der Pharm., **238**, 9 (1900).

The α-Derivative of Ethyl Hydrocinnamate and Sodium Benzoyldithiocarbamic Acid,



$$C_6H_5CO.N{=}C\begin{matrix}\diagup SNa \\ \diagdown SCH(CH_2C_6H_5)CO_2C_2H_5\end{matrix}$$

.—When, instead of using alcoholic solutions, the ethyl acetate derivative of benzoyldithiocarbamic acid is shaken with benzyl chloride, in the presence of an excess of aqueous alkali, the oily turbidity which results at first gives place to a yellow solid. On crystallizing this from alcohol, in which it is quite difficultly soluble, granular, well-developed, transparent, bright-yellow prisms are obtained. This material has no definite melting-point but decomposes a little above 100° with effervescence and is generally completely melted at 175°. The results of the analysis of this compound are as follows :

	Calculated for $C_{19}H_{18}O_3NS_2Na$.	Found.	
C	57.72	....	
H	4.55	4.20	
N	3.54	3.62	
S	16.20	16.40	16.0
Na	5.82	5.93	

When this material is suspended in water, in which it is quite difficultly soluble, and carbon dioxide is passed into the solution,

The α-Derivative of Ethyl Hydrocinnamate and Benzoyldithiocarbamic Acid, $C_6H_5CONHCS.SCH(CH_2C_6H_5)CO_2C_2H_5$, is liberated. This crystallizes from alcohol in bunches of bright-yellow prisms, which melt sharply at 79°. In other words, it has the same melting-point as its isomer described above, but when the two are mixed the melting-point is lowered to 63°. *The compounds prepared in the two ways, in this case, are isomeric and not identical.* Attempts to convert the ethyl acetate derivative of benzyl benzoylimidodithiocarbonate into the above sodium salt had no effect on the material. Since the acylimidodithiocarbonic esters do not form salts, and since this compound has a bright yellow color, it is in all probability a dithiourethane as named above. The results of the analysis are as follows :

	Calculated for $C_{19}H_{19}O_3NS_2$.	Found.
C	61.12	60.79
H	5.09	4.70
N	3.75	4.05

Phenyl thiocyanacetate, $NCS.CH_2CO_2C_6H_5$.—Thirty grams of chloracetyl chloride and 26 grams of phenol, when heated on the water-bath, until hydrogen chloride was no longer evolved, gave 28.5 grams phenyl chloracetate boiling at 123° to 128° at 13 mm. pressure. This material reacted immediately with an alcoholic solution of potassium thiocyanate. The product was an oil which slowly solidified ; it was then crystallized from dilute alcohol, whereupon it was obtained in colorless plates which showed signs of melting at 28° and then melted completely at 31° to 32°. A nitrogen determination gave :

	Calculated for $C_9H_7O_2NS$.	Found.
N	7.25	7.19

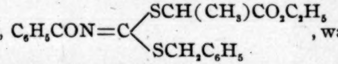
Phenyl Acetate Derivative of Benzoyldithiocarbamic Acid, $C_6H_5CONHCS.SCH_2CO_2C_6H_5$.—When the above rhodanide was warmed in a little benzene with thiobenzoic acid and then, after a few hours, allowed to cool, a shining mass of bright-yellow needles separated, which on crystallizing from alcohol melted at 127° to 129°, and an analysis gave the following result :

	Calculated for $C_{16}H_{13}O_3NS_2$.	Found.
N	4.36	4.25

Experiments in alcoholic solutions with this compound and benzyl chloride, and with phenyl chloracetate on benzylbenzoyldithiocarbamate, as well as methyl benzoyldithiocarbamate and ethyl chloracetate, did not yield satisfactory products, since oils and tars were formed.

The α-Derivative of Ethyl Propionate and Benzoyldithiocarbamic Acid, $C_6H_5CO.NHCS.SCH(CH_3)CO_2C_2H_5$, when crystallized from alcohol and benzene, forms acicular yellow prisms which melt at 144° to 145°. The nitrogen determination is as follows:

	Calculated for $C_{13}H_{15}O_3NS_2$.	Found.
N	4.71	5.00

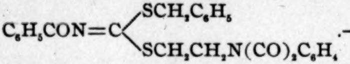
The α-Derivative of Ethyl Propionate and Benzylbenzoylimidodithiocarbonate,  $C_6H_5CON{=}C\begin{smallmatrix}\diagup SCH(CH_3)CO_2C_2H_5\\ \diagdown SCH_2C_6H_5\end{smallmatrix}$, was smoothly obtained in alcoholic solutions from benzyl benzoyldithiocarbamate and ethyl α-brompropionate. Prepared in this manner it forms colorless prisms, melting at 73° to 74°. The analytical results are as follows:

	Calculated for $C_{19}H_{20}O_3NS_2$.	Found.
C	62.01	61.09
H	5.42	5.58
N	3.61	3.67
S	16.53	16.83

When an attempt was made to prepare this compound from the α-derivative of ethyl propionate and benzoyldithiocarbamate and benzyl chloride, in alcoholic solution, a product was obtained, although in a less smooth manner than the above, which melted at 105° to 106°. After crystallizing from benzene and petroleum ether it formed stout, colorless prisms, which had a different appearance from the above. Whether the decided difference in melting-point of these two preparations is due to an impurity in one case, or to the fact that they are isomers, cannot be decided at present, since on repeating the preparation of the carbamate, from ethyl α-thiocyanpropionate in large quantities, a product of sufficient purity to convert into the imidoether was not obtained.

Phthalimidoethyl Benzoyldithiocarbamate, $C_6H_5CO.NHCS.SCH_2CH_2N(CO)_2C_6H_4$, forms fine, yellow needles, which are difficultly soluble in alcohol. When crystallized from chloroform it melted at 178° to 182°. It was converted directly into

Phthalimidoethyl Benzyl benzoylimidodithiocarbonate,



$$C_6H_5CON{=}C\begin{cases}SCH_2C_6H_5\\SCH_2CH_2N(CO)_2C_6H_4\end{cases}$$

.—This resulted smoothly when benzyl chloride acted on the sodium ethylate solution of the above. When crystallized from alcohol it forms beautiful colorless needles melting at 119° to 120°. A nitrogen determination gave:

	Calculated for $C_{25}H_{20}O_3N_2S_2$.	Found.
N	6.08	6.36

Attempts to prepare this compound from benzyl benzoyldithiourethane and bromethylphthalimide were without success. At ordinary temperatures the bromide does not react; when warmed in alcoholic solution, or when the urethane is treated with sodium and the bromide in benzene, decomposition occurs and benzyl rhodanide is formed.

Ethyl 1'-Thiocyanbenzene, $C_6H_5CH(SCN)CH_3$, from bromethylbenzene and potassium thiocyanate boiled for the most part at 157° to 159° at 36 mm. pressure. It formed a colorless oil which, on analysis, gave:

	Calculated for C_9H_9NS.	Found.
N	8.58	8.25

When this rhodanide was warmed with thiobenzoic acid no acyldithiourethane was formed. The product crystallized from alcohol in colorless prisms, melting constantly at 136° to 137°. It was insoluble in alkali, and a sulphur determination gave 17.74 per cent sulphur. The material was not further examined.

Desyl Thiocyanate, $C_6H_5COCH(SCN)C_6H_5$, results smoothly from bromdesoxybenzoin and alcoholic potassium thiocyanate. It crystallizes from alcohol in colorless prisms which melt at 110° to 111°. A nitrogen determination gave:

	Calculated for $C_{15}H_{11}ONS$.	Found.
N	5.53	5.55

An acyldithiourethane was not obtained when this rhodanide was heated in benzene solution with thiobenzoic acid.

The product was insoluble in alkali and crystallized from alcohol in colorless prisms which melted at 137°. A sulphur determination gave 18 per cent of sulphur. This compound was not further examined beyond establishing the fact that it is not desylthiolbenzoate, $C_6H_5CO.SCH(C_6H_5).COC_6H_5$ (melting-point 110° to 111°).

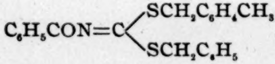
1′,m-Xylylthiocyanate $C_6H_4(CH_3)CH_2SCN$.—Metaxylyl bromide (boiling at 114° to 116° at 25 mm. pressure) readily reacts in alcoholic solution with potassium thiocyanate. The product is an oil which distils at 147° at 12 mm. pressure. It is colorless, has a disagreeable order and burning taste, but does not attack the eyes like the bromide. A nitrogen determination gave :

	Calculated for C_9H_9NS.	Found.
N	8.58	8.63

Metaxylyl Benzoyldithiocarbamate, $C_6H_5CO.NHCS.SCH_2C_6H_4CH_3$.—The above rhodanide and thiobenzoic acid readily combine when heated on the water-bath for several hours in benzene solution. The product is difficultly soluble in cold alcohol, readily in hot, from which it crystallizes in bright-yellow, needle-like prisms melting at 93° to 94°. A nitrogen determination gave :

	Calculated for $C_{16}H_{15}ONS_2$.	Found.
N	4.65	4.73

Benzylmetaxylyl Benzoylimidodithiocarbonate,



$$C_6H_5CON{=}C\begin{cases}SCH_2C_6H_4CH_3\\SCH_2C_6H_5\end{cases}$$

.—When benzyl benzoyldithiocarbamate, sodium ethylate, and *m*-xylyl bromide were mixed in alcoholic solution, a reaction took place almost immediately, and the liquid became filled with a mass of bulky, colorless crystals. These were washed with water and crystallized three times from alcohol, whereupon they showed the constant melting-point of 97° to 98°. A nitrogen determination gave :

	Calculated for $C_{23}H_{21}ONS_2$.	Found.
N	3.58	3.69

On the other hand, when *m*-xylyl benzoyldithiocarbamate, sodium ethylate, and benzyl chloride were allowed to react, under precisely similar conditions to the above, the reaction took place much more slowly. When the two experiments were performed at the same time, the one above appeared to be complete before the latter separated any crystals. That the reaction was less smooth in this case was shown by the solution taking on a yellow color. After standing over night water precipitated a solid, which, after being crystallized six times from alcohol, melted for the most part at 85° to 86°, but did not become clear until 89°.5. It appeared that the melting-point of the material could not be altered by crystallizing from alcohol. A second experiment with carefully purified material gave the same result. Were it not for the fact that the material did not melt like a pure compound, it would be taken for an isomer of the ester melting at 97° to 98°.

In our next experiment, *m*-xylyl benzoyldithiocarbamate was dissolved in an excess of dilute aqueous sodium hydrate and shaken with benzyl chloride. A solid was thus obtained which after one or two crystallizations from alcohol melted sharply at 97° to 98°, and when mixed with the material of the same melting-point, prepared in the other way, the melting-point was not altered. The products proved to be identical in every respect. The fact was also established that this compound smoothly results when benzyl benzoyldithiocarbamate was treated in aqueous alkali with *m*-xylyl bromide.

Some attempts were made to determine exactly what impurity is present in the ester melting at 85° to 89°.5 by mixing various substances with the pure product melting at 97° to 98°. For example, the xylyl urethane, benzoyl disulphide, benzyl disulphide, benzylthiolbenzoate, etc. A product melting constantly at 85° to 89°.5, however, was not obtained.

Metaxylyl mercaptan, $CH_3C_6H_4CH_2SH$, forms a colorless oil with a disagreeable odor, which boils from 215° to 217° at ordinary pressures. A sulphur determination gave:

	Calculated for $C_8H_{10}S$.	Found.
S	23.18	22.88

This compound was converted into

Metaxylyl benzyl sulphide, $CH_3C_6H_4CH_2SCH_2C_6H_5$, which proved to be a colorless oil boiling at 193° to 196° at 15 mm. pressure. The product of the action of iodine on the alkaline solution of the above mercaptan (xylyl disulphide) was also obtained in the form of an oil. A sulphur determination in the case of metaxylyl benzyl sulphide gave:

	Calculated for $C_{15}H_{16}S$.	Found.
S	14.0	14.3

Dixylyl benzoylimidodithiocarbonic ester was smoothly formed in alcoholic solutions. It forms colorless prisms from alcohol which melt at 89°.5 to 90°. A nitrogen determination gave:

	Calculated for $C_{24}H_{23}ONS_2$.	Found.
N	3.45	3.51

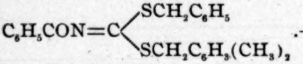
Mesityl thiocyanate, $(CH_3)_2C_6H_3CH_2SCN$, results smoothly from mesityl bromide and alcoholic potassium thiocyanate. It is very soluble in strong alcohol; from dilute, it forms beautiful colorless plates, which melt at 58°. A nitrogen determination gave:

	Calculated for $C_{10}H_{11}NS$.	Found.
N	7.90	7.78

Mesityl Benzoyldithiocarbamate, $C_6H_5CONHCS.SCH_2C_6H_3(CH_3)_2$.—The crude product in this case was an oil, which was treated with sodium hydrate, and from the alkaline solution the urethane was precipitated by means of carbon dioxide. It crystallizes from alcohol in yellow plates or leaflets, which melt at 114°.5. A nitrogen determination gave:

	Calculated for $C_{17}H_{14}ONS_2$.	Found.
N	4.44	4.46

Benzyl mesityl benzoylimidodithiocarbonate,



$$C_6H_5CON{=}C\begin{cases}SCH_2C_6H_5\\SCH_2C_6H_3(CH_3)_2\end{cases}$$

.—The reaction in the case of benzyl benzoyldithiocarbamate, sodium ethylate, and mesityl bromide was practically complete in thirty minutes, and was perfectly smooth. This ester, on crystallizing from alcohol, formed prisms which melted at 117°.5. A nitrogen determination gave :

	Calculated for $C_{24}H_{23}ONS_2$.	Found.
N	3.23	3.25

When, under precisely similar conditions, mesityl benzoyldithiocarbamate (3 grams), sodium ethylate, and benzyl chloride were allowed to react, there was only a slight turbidity to indicate a reaction, after standing twelve hours. Water then precipitated an oil (small amount), and on passing carbon dioxide into the aqueous alkaline solution unaltered urethane (1.5 grams) was precipitated.

On the other hand, the imido ester results with the greatest ease, and in a few minutes, on simply shaking the aqueous alkaline solution of mesityl benzoyldithiocarbamate with benzyl chloride. The product had all the properties of the above ester melting at 117°.5.

From the results with xylyl and mesityl urethanes it might seem that aqueous solutions in general are more favorable than alcoholic for the preparation of acylimidodithiocarbonic esters, but this is not true, since it was found that ethyl chloracetate and ethyl α-brompropionate did not give imido esters with benzylbenzoyldithiourethane, while in alcoholic solution the esters are smoothly formed.

NEW HAVEN, CONN., April 22, 1901.

REVIEWS.

Chemical Lecture Experiments. By Francis Gano Benedict, Ph.D., Instructor in Chemistry in Wesleyan University. New York: The Macmillan Company; London: Macmillan & Co., L't'd. 1901. pp. 436 + xiii. Price, $2.00.

This is an attractive book that is likely to prove valuable to teachers of chemistry. The directions are clear, so that any one with proper training can follow them. The author says: "The object of this book is primarily to furnish teachers with a large number of reliable lecture experiments. That these experiments require in many cases different treatment from those performed in the laboratory will be obvious when it is considered that the demonstrations on a lecture-table must be of sufficient magnitude and of a character marked enough to enable the phenomenon to be observed at as great a distance as possible." * * * "All experiments requiring especially elaborate apparatus have here been rigorously excluded." * * * "The material here presented has been prepared with reference also to its use by students desiring collateral reading in connection with experimental lectures. As an elaboration of the laboratory manual the book may also be used by students for the preparation of many compounds not considered in elementary text-books."

A copy of the book should be available wherever chemistry is taught.

Laboratory Instructions in General Chemistry. Arranged by Ernest A. Congdon, Ph.B., F.C.S., Professor of Chemistry, Drexel Institute, Philadelphia. With 56 illustrations. Philadelphia: P. Blakiston's Son & Co. 1901. pp. 110. Price, $1.00.

This contains directions for laboratory work by students and, while it necessarily has much in common with other books prepared for the same purpose, it is distinguished by the evident care taken by the author in devising his experiments and in writing his directions. He says: "Much of the material is original, having been developed in the course of ten years' experience in laboratory teaching, while those portions taken from other sources have been modified and added to, so that they might better meet the wants of students."

Some of the experiments are rather difficult for a beginner, but that objection can be made to every course that has been prepared. With a good teacher and with plenty of time this course could be followed with profit.

An Elementary Treatise on Qualitative Chemical Analysis. By J. F. Sellers, A.M., Professor of Chemistry, Mercer University, Georgia. Boston: Ginn & Company. pp. v + 160.

This book is a new applicant for favor in a field already well occupied; but the work has distinctive merits. The author has consulted the latest and highest authorities on each topic; he has used good judgment in the selection of the matter of the book and in the quantity of matter introduced, thereby making the volume one of practical size and contents for the college student of qualitative analysis, who expects to proceed to quantitative work.

The methods of separation and proof are clearly stated, and they are generally those most approved by the best authorities. The author is careful fully to set forth the scientific principles on which processes depend; illustrative reactions are given wherever necessary; the teaching is so rationally and practically blended as to make dextrous and scientific workers.

More attention than usual in books of this size is devoted to the subjects of solution, osmosis, electrolytic dissociation, spectroscopy.

The book is full of valuable suggestions for the guidance of students in the care and use of apparatus, reagents, furniture.

R. W. Jones.